Utilization of highly robust and selective crosslinked polymeric ionic liquid-based sorbent coatings in direct-immersion solid-phase microextraction and high-performance liquid chromatography for determining polar organic pollutants in waters

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Abstract

Several crosslinked polymeric ionic liquid (PIL)-based sorbent coatings of different nature were prepared by UV polymerization onto nitinol wires. They were evaluated in a direct-immersion solid-phase microextraction (DI-SPME) method in combination with high-performance liquid chromatography (HPLC) and diode array detection (DAD). The studied PIL coatings contained either vinyl alkyl or vinylbenzyl imidazolium-based (ViC_nIm- or ViBC_nIm-) IL monomers with different anions, as well as different dicationic IL crosslinkers. The analytical performance of these PIL-based SPME coatings was firstly evaluated for the extraction of a group of 10 different model analytes, including hydrocarbons and phenols, while exhaustively comparing the performance with commercial SPME fibers such as polydimethylsiloxane (PDMS), polyacrylate (PA) and polydimethylsiloxane/divinylbenzene (PDMS/DVB), and using all fibers under optimized conditions. Those fibers exhibiting a high selectivity for polar compounds were selected to carry out an analytical method for a group of 5 alkylphenols, including bisphenol-A (BPA) and nonyl-phenol (NP). Under optimum conditions, average relative recoveries of 108% and inter-day precision values (3 non-consecutive days) lower than 19% were obtained for a spiked level of 10 µg·L⁻¹. Correlations coefficients for the overall method ranged between 0.990 and 0.999, and limits of detection were down to 1 µg·L⁻¹. Tap water, river water, and bottled water were analyzed to evaluate matrix effects. Comparison with the PA fiber was also performed in terms of analytical performance. Partition coefficients (log K_{fs}) of the alkylphenols to the SPME coating varied from 1.69 to 2.45 for the most efficient PIL-based fiber, and from 1.58 to 2.30 for the PA fiber. These results agree with those obtained by the normalized calibration slopes, pointing out the affinity of these PILs-based coatings.

41 **Keywords:** ionic liquids; polymeric ionic liquids; crosslinked polymers; solid-phase
42 microextraction; high-performance liquid chromatography; alkylphenols

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1. Introduction

Solid-phase microextraction (SPME) is a successful extraction and preconcentration technique developed by Pawliszyn [1]. It involves a number of interesting characteristics such as simplicity, easiness of automation, high enrichment factors, and environmental-friendliness. SPME is solvent-free in gas-chromatography (GC) applications and requires microliters of organic solvents for desorption in liquid chromatography (LC) and capillary electrophoresis (CE). The main disadvantage that can be attributed to the technique is the limited number of commercially-available SPME coatings. In this sense, recent efforts in SPME research have been devoted to the design and implementation of novel coating materials that are able to achieve selectivity for certain analytes and offer high robustness [2].

Several materials have been suggested as novel coatings for SPME including molecularly imprinted polymers [3], single- and multiwalled-carbon nanotubes [4], graphene [5], metallic nanoparticles [6], nanoporous silica [7], and metal-organic frameworks [8], among others. It is fair to recognize that ionic liquids (ILs) [9] and polymeric ionic liquids (PILs) [10] are among these materials most extensively studied in SPME due to their high chemical and thermal stability, adequate viscosity, and tunable selectivity through simple chemical modifications [11].

Anderson's group firstly demonstrated the performance of PILs as coating materials for SPME in 2008 [12]. Since then, a number of studies have demonstrated the use of PILs as sorbent coatings in headspace (HS)-SPME-GC applications, with the ability to resist temperatures up to 250 °C [13,14,15]. In 2010, the stability of PILs coatings prepared in the same manner was further demonstrated when used in DI-SPME-GC applications [16], and further used in a number of other studies [17,18].

As an advance in the preparation of more stable coatings, SPME fibers were prepared by chemically linking the PIL to the fiber support. The bonding was ensured by proper treatment and derivatization of a stainless steel support, via silver layer deposition [19,20] or gold layer deposition [21], and further functionalization. In 2012, the utility of crosslinked PILs in HS-SPME was also described [22], with important attributes of higher thermal stability and prolonged fiber life-time, also taking advantage of the silver layer deposition onto stainless steel. PIL coatings in HS-SPME using an IL monomer and a dicationic IL crosslinker, with titanium fibers anodized and derivatized as supports, have also been described [23].

The development of a novel on-fiber co-polymerization method assisted by UV light for the preparation of crosslinked PIL-based SPME coatings was described in 2012 [24]. In this method, the co-polymerization of the IL together with the cross-linking agent takes place on the fiber support (fused silica) and inside a UV reactor, which enormously speeds up the preparation of fibers. PIL-based SPME fibers prepared with this procedure were used in HS-SPME-GC [25,26]. Nitinol fibers have been also used as supports with the same polymerization approach for SPME-GC [27], generating highly robust coatings. More recently, nitinol supports prepared with the UV method of polymerization have been mounted onto commercial SPME devices and used in an automated DI-SPME-GC approach [28].

The wide majority of PIL-SPME works have been carried out in combination with GC. Few studies have described the use of PIL-based SPME with HPLC. Among them, the use of functionalized PIL monolithic sorbent materials onto hollow-fiber supports of polyvinylidene fluoride (PVDF) [29] or polythene (PE) [30] has been reported. Furthermore, the use of multiple monolithic SPME fibers based on a PIL has also been recently reported, allowing the decrease of extraction times [31]. Chen *et al.*

developed a SPME fiber for HPLC based on the PIL obtained using the IL monomer 1-vinyl-3-hexadecylimidazolium hexafluorophosphate and polyhedral oligomeric silsesquioxane as crosslinker, mounted onto the surface of an anodized Ti wire [32]. More recently, Yu *et al.* developed a neat PIL for DI-SPME-HPLC, using both a monocationic IL monomer and a dicationic IL as a crosslinker onto nitinol supports [33]. The coatings exhibited high stability in acidic media as well as in presence of several organic solvents.

The main goal of the present work is the development of novel neat crosslinked PIL-based SPME coatings for use in DI-SPME mode in combination with HPLC. Four different highly crosslinked PIL-based coatings have been prepared onto nitinol wires and examined with a wide variety of analytes, with the purpose of evaluating their quality analytical parameters. Those fibers exhibiting higher selectivity for endocrine disrupting phenols were selected for the validation of an analytical method, and were thoroughly compared to commercial SPME coatings in the analysis of real aqueous samples.

2. Experimental

2.1. Chemicals, reagents and samples

The model analytes included in the preliminary screening study were: carbamazepine (Cmz), benzaldehyde (Bnzal), bisphenol A (BPA), 2-nitrophenol (NP), $\alpha,\alpha,\alpha,6$ -tetrafluoro-*m*-toluidine (tfTol), 3-*tert*-butylphenol (*t*-BuP), ethyl benzoate (EB), naphthalene (Nap), gemfibrozil (Gfz), and irgasan (Irg). These analytes were purchased from Sigma-Aldrich (St. Louis, MO, USA). Individual standard solutions were prepared

in acetonitrile at a concentration of $10 \text{ mg}\cdot\text{mL}^{-1}$. Individual solutions with intermediate concentrations were also prepared by dilution with acetonitrile. All solutions were stored at 4°C . Intermediate standard solutions were used in the preparation of aqueous working solutions (10 mL) containing all compounds at concentrations ranging from 0.5 to $500 \text{ }\mu\text{g}\cdot\text{L}^{-1}$.

The analytes included in the quantitative study were: bisphenol A (BPA), 4-cumylphenol (CuP), 4-*tert*-octylphenol (*t*-OP), and 4-octylphenol (OP), which were purchased from Sigma-Aldrich (Steinheim, Germany), and 4-*n*-nonylphenol (*n*-NP), which was supplied by Alfa Aesar (Karlsruhe, Germany). In this case, individual standard solutions ($1000 \text{ mg}\cdot\text{L}^{-1}$) were prepared in acetonitrile. An intermediate standard solution containing all alkylphenols ($50 \text{ mg}\cdot\text{L}^{-1}$, in acetonitrile) was prepared weekly. All solutions were stored at 4°C . Working solutions in ultrapure water (18 mL) were prepared containing all alkylphenols at concentration levels ranging from 5 to $200 \text{ }\mu\text{g}\cdot\text{L}^{-1}$.

The reagents used to synthesize ILs and PILs were: acrylonitrile, 1-bromohexadecane, 1-chlorohexane, 1,12-dibromodecane, 2-hydroxy-2-methylpropiophenone (DAROCUR 1173), imidazole, 4-vinylbenzyl chloride, 1-vinylimidazole, and vinyltrimetoxysilane (VTMS). They were acquired from Sigma-Aldrich (St. Louis, MO, USA). Lithium bis[(trifluoromethyl)sulfonyl]imide (Li-NTf₂) was obtained from SynQuest Laboratories (Alachua, FL, USA). Chloroform, sodium hydroxide, hydrogen peroxide (30% w/w), HPLC-grade methanol, isopropanol, and 2-propanol, were supplied by Fisher Scientific (Fair Lawn, NJ, USA).

Ultrapure water ($18.2 \text{ m}\Omega\cdot\text{cm}$) was obtained from a Milli-Q gradient A10 system (Millipore, Bedford, MA, USA). Acetic acid and HPLC-grade acetonitrile were

supplied by Sigma-Aldrich (Steinheim, Germany). Methanol (HPLC-grade) and hydrochloric acid (36.5-38%) were obtained from Fisher Scientific.

Different samples were employed depending on the group of analytes under study. Thus, for the model analytes, recovery studies were accomplished in tap water sample obtained from the laboratory (OH, USA) and in river waters collected from the Maumee River in Maumee (OH, USA). The river water samples were filtered through a 3 mL syringe with 0.45 μm filter units (Fisher Scientific). For alkylphenols, tap water collected in the laboratory (Tenerife, Canary Islands) was used to evaluate matrix effect. Tap water was also subjected to heating, and then used to fill empty water plastic bottles obtained from local markets. These plastic bottles had the resin identification code number 7, which refers to polycarbonate, polylactic acid, and acrylic plastics, among others. The purpose was to assess if migration of the alkylphenols from the plastic bottle occurred. A bottled water sample acquired from a local market was also analyzed.

2.2. Materials

Elastic nitinol wires with an external diameter of 127 μm were employed as solid support for SPME fibers, being supplied by Nitinol Devices & Components (Fremont, CA, USA). The SPME fiber assemblies were provided by Supelco (Bellefonte, PA, USA). The commercial fibers: 85 μm polyacrylate fiber (PA), 100 μm polydimethylsiloxane fiber (PDMS), and 60 μm polydimethylsiloxane/divinylbenzene fiber (PDMS/DVB), were also acquired from Supelco.

The DI-SPME procedure for the model analytes was performed in 10 mL amber glass vials with screw caps and polytetrafluoroethylene (PTFE)/silicon septa, purchased from Supelco. The DI-SME for alkylphenols was carried out in 20 mL amber glass vials

with screw caps and PTFE/Butyl septa, from Agilent Technologies (Santa Clara, CA, USA); using magnetic stir bars of 15×4.5 mm (Sigma-Aldrich, Steinheim, Germany) and a magnetic stirrer from IKA® (IKA Instruments Werke GmbH & Co. KG, Staufen, Germany).

The desorption step was performed *off-line* by placing the fiber into a sealed end 10-100 µL pipet tip (Fisher Scientific) for the model analytes. Glass inserts of 0.25 mL from Supelco, which were placed into amber glass vials of 2 mL in volume from Agilent Technologies, were used for the *off-line* desorption of the alkylphenols.

2.3. Instrumentation

A RPR-100 reactor provided with a spinning carousel, used for UV polymerization of PILs, was obtained from Southern New England Ultraviolet Company (Bradford, CT, USA).

The preliminary study was carried out using a LC-20A liquid chromatograph (Shimadzu, Japan) provided with a SPD-20 UV/VIS detector. A C₁₈ column (250 mm × 4.6 mm × 5 µm) from Restek (Bellefonte, PA, USA) and a guard column (KromasilTM C₁₈, 5 µm) were employed. The separation of the model analytes was performed utilizing acetonitrile and water containing 0.1% (v/v) of acetic acid, at a flow rate of 1 mL·min⁻¹. The separation gradient began at 50% (v/v) acetonitrile and was increased to 90% (v/v) in 25 min. The UV detection was accomplished at 254 nm for this group of analytes. The chromatographic method allowed the baseline separation of the 10 model analytes in less than 22 minutes as shown in Figure S1 (A).

A 1260 Infinity HPLC with diode array detection (DAD) from Agilent Technologies was employed in the determination of alkylphenols. ACE UltraCore 5

SuperC18 column (150 mm × 4.6 mm × 5 μm) was supplied by Symta (Madrid, Spain). Acetonitrile and ultrapure water containing 0.4% (v/v) of acetic acid were used as mobile phase at a flow rate of 1 mL·min⁻¹. The separation gradient employed for the separation of the alkylphenols started at 50% (v/v) of acetonitrile and was then increased to 100% (v/v) for 5 min, being finally held for 3 additional minutes. The quantification wavelength was 280 nm. The chromatographic method allowed the baseline separation of the alkylphenols in less than 8 minutes as shown in Figure S1 (B).

2.4. Procedures

2.4.1. Synthesis of the ILs monomer and the dicationic IL crosslinkers

The preparation of ILs monomer: 1-vinylbenzyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide (ViBC₁₆Im-NTf₂), 1-vinyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide (ViC₁₆Im-NTf₂), 1-vinyl-3-hexadecylimidazolium bromide (ViC₁₆Im-Br), and 1-vinyl-3-hexylimidazolium chloride (ViC₆Im-Cl), was performed according to previously reported procedures [12,17]. The synthesis of the dicationic ILs: 1,12-di(3-vinylimidazolium)dodecane bromide ((ViIm)₂C₁₂-2Br), 1,12-di(3-vinylimidazolium)dodecane bis[(trifluoromethyl)sulfonyl]imide ((ViIm)₂C₁₂-2NTf₂) and 1,12-di(3-vinylbenzylimidazolium)dodecane bis[(trifluoromethyl)sulfonyl]imide ((ViBIm)₂C₁₂-2NTf₂) was carried out also following reported procedures [25,34].

2.4.2. Fabrication of PIL-based SPME fibers

PIL-based sorbent coatings utilized in this work were prepared onto a nickel-titanium metal alloy wires according to the UV copolymerization method published by Ho *et al.* [27]. Prior to co-polymerization, some modifications were carried out on the metal support. First, the wire was immersed in a solution of hydrogen peroxide (30% w/w) for 2 h at 72 °C to functionalize the surface of the metallic support with hydroxyl groups. Then, the fiber was reacted with VTMS for 2 h at 85 °C to functionalize the surface of the support with the organosilane. This procedure ensures a chemical linkage between the support and the PIL, which is later coated on the support.

For each PIL, once both ILs (the monomer and the crosslinker) were synthesized, the co-polymerization process was carried out on the metallic modified support. The polymerization consists of dip-coating 1 cm of the fiber with a solution containing the IL monomer, the dicationic IL crosslinker (in a 50:50 w/w ratio respect to the IL monomer), and the free-radical initiator DAROCUR 1173 (3%, w/w). Then, the fiber is subjected to UV radiation ($\lambda = 254$ nm for 2 h for halide-based PILs, and $\lambda = 360$ nm for 30 min for NTf₂-based PILs) in the reactor. Finally, the fiber was mounted using the commercial SPME fiber assemblies from Supelco. Conditioning of the PIL-based fibers was performed by immersion in 50 μ L of methanol for 30 minutes (this step was also used to ensure absence of polymer bleeding). Table 1 shows the chemical composition of the PIL-based fibers utilized in this work as SPME coatings for HPLC.

2.4.3. DI-SPME-HPLC-DAD method

The fiber was directly immersed into the aqueous solution containing the analytes. The extraction was carried out at room temperature under a constant agitation rate of 500 rpm. The *off-line* desorption step was accomplished by exposing the fiber to a small volume of desorption solvent: 50 μ L in a pipet tip for the model analytes, and

250 μL for alkylphenols. Then, 20 μL of desorption solvent was subjected to HPLC separation. All DI-SPME experiments were manually performed (without any autosampler), ensuring the same immersion depth in all cases. After every extraction/desorption cycle (for PIL-based and commercial fibers), a single cleaning step was carried out in 1.5 mL of methanol for 15 min to avoid memory effects.

2.4.4. Estimation of partition coefficients

In any SPME procedure, analytes partition between the sample and the sorbent coating until equilibrium conditions are achieved. The partition coefficient of the analyte (K_{fs}) can be estimated according to the following equation [17]:

$$K_{fs} = \frac{V_s}{V_f \left(\frac{n_0}{n_f} - 1 \right)} \quad \text{Equation 1}$$

In equation 1, n_0 is the initial amount of analyte in the sample (in mg) while n_f indicates the amount of analyte on the fiber once the equilibrium is reached. n_f values can be calculated using the chromatographic calibrations (obtained in absence of DI-SPME experiences), using the peak area obtained after a n_0 initial amount of analytes which is subjected to the whole DI-SPME-HPLC method. In this equation, V_s indicates the sample volume (18 mL for alkylphenols), and V_f represents the volume of the sorbent coating, which can be calculated using the radius of the fiber coating and the coating length (1 cm). The V_f values obtained for the PIL-based sorbent coatings employed for the determination of alkylphenols were 0.283 μL for both PIL-1b and PIL-4. The V_f value for the commercial PA fiber was obtained from Supelco, being 0.520 μL .

3. Results and discussion

3.1. Performance of the PIL-based sorbent coatings with model analytes

The PIL-based fibers developed for DI-SPME-HPLC were first examined with a group of 10 different model analytes including polar analytes such as BPA and non-polar analytes such as Nap. In this preliminary study, fibers PIL-1a, PIL-2 and PIL-3, with a film thickness of approximately 14 μm , were evaluated together with a number of commercial SPME fibers compatible with HPLC analysis. The main goal at this point is to test the influence of the nature of the sorbent coating without considering differences in thicknesses. In initial experiments, 10 mL of aqueous working solutions containing the analytes at concentrations ranging from 10 to 400 $\mu\text{g}\cdot\text{L}^{-1}$ were subjected to the overall method in triplicate. The nature of the desorption solvent, desorption time, extraction time, and pH of the sample, were evaluated as the main parameters. The obtained peak areas were used as the response to assess the extraction efficiency of the method. After optimization, a comparison among all coatings was performed.

3.1.1. Optimization of the DI-SPME-HPLC method using all sorbent coatings

Some parameters affecting the method were previously fixed to ensure high sensitivity, such as the volume of the aqueous sample (10 mL), the volume of desorption solvent in *off-line* mode (50 μL , to ensure complete immersion of the fiber) and the agitation rate (500 rpm, to guarantee the integrity of the fiber while stirring as well as an adequate homogenization of the sample). The main parameters influencing the extraction efficiency of the DI-SPME method were also studied, and include the extraction time, the pH of the sample, the nature of desorption solvent, and the desorption time,. The optimization followed a simple factor by factor approach. The Figures S2, S3, S4, S5, S6 and S7 of the Electronic Supplementary Material (ESM) include all studies carried out in the optimization for the model analytes with all fibers.

According to the results observed, the optimum conditions selected were: methanol as desorption solvent for PIL-based, PA and PDMS/DVB fibers, and acetonitrile for PDMS fiber; desorption time of 30 min for commercial fibers, PIL-1a and PIL-3, and 40 min for fiber PIL-2; extraction time of 45 min for all the SPME fibers as a compromise in order to benefit most analytes; and pH value of 2 for all PILs and commercial fibers.

3.1.2. Evaluation of extraction efficiency for PIL-based sorbent coatings and commercial fibers

Once the DI-SPME-HPLC method was optimized for each fiber, the extraction efficiency of each sorbent coating was examined by comparing the peak area obtained for the model analytes. Figure 1 shows a comparison between PIL-based fibers and commercial fibers using the normalized peak area (peak area divided by the coating thickness) [16] to focus on fiber nature and not the effect exerted by the film thicknesses. The PIL-1a fiber exhibited higher selectivity for aromatic compounds such as Cmz and Nap, which may be due to the vinyl benzyl moiety within the cation that enhances π - π interactions with these analytes [35]. It can be also clearly observed that fiber PIL-3 provides higher affinity for polar compounds such as BPA and tfTol. This may be related to the anionic component of the fiber as it is known that halide anions exhibit higher hydrogen bond basicity leading to stronger hydrogen bonding interactions with polar analytes [15]. Hence, it can be concluded that PIL-based sorbent coatings offer an interesting tunable selectivity for a wide range of compounds depending on their chemical composition.

The PDMS/DVB fiber was the best commercial fiber and exhibited significantly higher extraction efficiencies for model analytes in comparison with the other fibers

studied. However, the PA fiber was more suitable for the extraction of highly polar analytes such as BPA. Poor extraction efficiency was shown for the PDMS fiber which was not able to extract BPA or NP. For these reasons, only the PA and PDMS/DVB commercial fibers were selected for a further comparative study with the PIL-based sorbent coatings.

3.1.3. Analytical performance of all sorbent coatings

The validation of the optimized DI-SPME-HPLC method was performed for the PA, PDMS/DVB and PIL-based fibers with the model analytes. The analytical quality parameters including linear ranges, sensitivities (slopes), correlation coefficients (R) and limits of detection (LODs) are listed in Table 2 for PIL-based fibers. All calibrations provided high correlation coefficients varying from 0.990 to 0.999 within the linear ranges studied. The maximum sensitivity (evaluated as the calibration slope) was found for Irg when using all the PIL-based fibers. As it was predicted in the previous comparative study, the PIL-1a fiber exhibited a better sensitivity for aromatic compounds while the PIL-3 fiber containing the hydrogen basic bromide anion is more suitable for polar compounds. The PIL-2 fiber showed higher slope values for Bnzal, t-ButP, Gfz and Irg in comparison with the other fibers. The LODs were calculated as three times the signal to noise ratio, and were validated by decreasing the analyte concentration of a standard until this ratio was achieved. The lowest LODs were found for Irg with a value of $2 \mu\text{g}\cdot\text{L}^{-1}$ using the PIL-2 fiber. The overall LODs were in a range of $2.5\text{-}20 \mu\text{g}\cdot\text{L}^{-1}$ for PIL-1a, $2\text{-}20 \mu\text{g}\cdot\text{L}^{-1}$ for PIL-2 and $2.5\text{-}20 \mu\text{g}\cdot\text{L}^{-1}$ for PIL-3. It is important to point out that these LODs values are satisfactory considering that a UV/Vis detector was employed.

Table S1 from the ESM contains the analytical quality parameters obtained with the PA and PDMS/DVB commercial fibers. The PDMS/DVB fiber showed better sensitivities for all analytes except for BPA if compared with the PA and PIL-based fibers. Thus, wider ranges and lower LODs ranging from 0.2 to 10 $\mu\text{g}\cdot\text{L}^{-1}$ were obtained for the PDMS/DVB fiber. With regards to the polar PA fiber, a higher slope was found for BPA while the LODs oscillated between 1 and 25 $\mu\text{g}\cdot\text{L}^{-1}$. In all cases, the correlation coefficients were higher than 0.996. In general, commercial fibers provide better sensitivities for model analytes than PIL-based sorbent coatings due to their higher film thickness. However, PIL-based fibers showed much better sensitivities and lower LODs for Cmz and NP in comparison with the PA fiber, and for BPA compared to the PDMS/DVB coating.

3.1.4. Recovery and precision studies in real water samples

In order to prove the applicability of the DI-SPME-HPLC method using PIL-based fibers for the analysis of real samples, studies examining the intra-day precision (as RSD) and relative recovery (RR in %) were carried out for the model analytes tested. This study was performed at two different spiked levels in both river and tap water samples subjected to the overall method ($n = 3$): 40 $\mu\text{g}\cdot\text{L}^{-1}$ and 200 $\mu\text{g}\cdot\text{L}^{-1}$. Only the PIL-1a and PIL-2 fibers were tested since both of them showed satisfactory analytical performance for most analytes.

The results included in Table S2 of the ESM show that the PIL-2 fiber provides a little better relative recovery values at both concentration levels in both water samples, with average values of 91.2% at 40 $\mu\text{g}\cdot\text{L}^{-1}$ and 95.1% at 200 $\mu\text{g}\cdot\text{L}^{-1}$ in river waters, and 85.9% at 40 $\mu\text{g}\cdot\text{L}^{-1}$ and 93.8% at 200 $\mu\text{g}\cdot\text{L}^{-1}$ in tap waters. In the case of the PIL-1a fiber, poor values of relative recovery are found for NP, with average values lower than

68% at both concentration levels in both water samples. However, the recovery results obtained for NP using both PIL fibers are adequate since commercially available SPME fibers cannot even extract this kind of analytes from real water samples when they are combined with liquid chromatography [36].

The RSD values for the PIL-1a fiber in both samples ranged from 2.9 to 15% at 40 $\mu\text{g}\cdot\text{L}^{-1}$, and from 3.7 to 16% at 200 $\mu\text{g}\cdot\text{L}^{-1}$. With regard to the PIL-2 fiber, the overall RSD values were lower in both water samples, varying in the ranges 0.5-18% at 40 $\mu\text{g}\cdot\text{L}^{-1}$, and 0.7-14% at 200 $\mu\text{g}\cdot\text{L}^{-1}$.

All of these results highlight that crosslinked PIL-based SPME fibers are suitable in SPME-HPLC applications for the determination of a broad range of compounds in real water samples with adequate analytical performance (extraction efficiency, sensitivity, reproducibility, and analysis of real samples). Moreover, it is also important to point out that PIL-based fibers are able to perform with adequate reproducibility while resisting the dissolution or sloughing from the support when organic solvents are used as desorption solvents (up to ~100 extraction-desorption steps), and also at low pH values.

3.2. Application of PIL-based sorbent coatings for the analysis of alkylphenols

Considering the results obtained in the preliminary study, several PIL-based fibers were selected for the determination of alkylphenols. Five polar disrupting endocrine alkylphenols, including BPA, CuP, t-OP, OP and n-NP, were chosen. Given the polarity of these compounds as well as the presence of an aromatic ring in their structure, fibers similar to the PIL-1a and PIL-3 coatings were employed. Hence, two new fibers were developed in an attempt to obtain the desired selectivity. These fibers include PIL-1b, which is identical to PIL-1a but with a higher film thickness (~35 μm);

and PIL-4 (~35 μm), which possesses a similar chemical composition as PIL-3 except for a shorter side chain in the cationic moiety of the monomer as well as the presence of chloride anion instead of bromide as anion within the monomer. The presence of chloride anion has been shown to increase sensitivity and selectivity for polar compounds [15]. It is also important at this point to make the comparison not only centered on the nature of the coatings but also on the thicknesses, and thus efforts were shifted to get thicker coatings. Thicker coatings were obtained for these fibers by employing a recently developed “spin coating” method [37]. Figure S8 from ESM illustrates the cross-section of selected PIL-based coatings prepared in this study, where the different film thicknesses for PIL-1a (Figure S8 (A)) and PIL-1b (Figure S8 (B)) can be observed.

The commercial PA fiber was also evaluated for the analysis of alkylphenols to carry out an exhaustive comparative study. The selection of this commercial coating is based on its polar nature along with the fact it is the most common SPME fiber employed for the analysis of these compounds [38].

The separation of the five analytes was attained in 7 min using the conditions described in section 2.3 (Figure S1 of the ESM). The *off-line* desorption step was performed by immersing the fiber into 250 μL of methanol, which was the best desorption solvent for PIL-based coatings in the preliminary study with model analytes. In this case, pH of the sample, extraction time, and desorption time were examined in order to optimize the overall method with this specific group of analytes. The experiments were performed in triplicate using 18 mL of aqueous standards at a concentration level of 200 $\mu\text{g}\cdot\text{L}^{-1}$.

3.2.1. Optimization of the DI-SPME-HPLC-DAD method

The analytes employed in this work are considered to be weakly acidic. Thus, it is necessary to work at low pH values to improve the extraction efficiency. The effect of the sample pH was examined at two pH conditions: pH 2 and pH 5. As shown in Figure S9 from ESM, in general, the best results were obtained when the pH was adjusted at a value of 2 for all fibers.

The extraction time profiles were obtained for all of the SPME fibers and are included in the Figure S10 (left side) from ESM. With regard to the PIL-based fibers, it is observed that most analytes have an optimum equilibrium time of ~ 60 min for PIL-1b and ~ 45 min for PIL-4. In the case of the PA fiber, an equilibrium time of ~ 45 min was obtained except for OP and n-NP, which needed extraction times longer than 60 min. Based on these results, the optimum extraction times selected were 45 min for the PIL-4 and PA fibers, and 60 min for the PIL-1b fiber.

The desorption time was evaluated between 5 and 20 min to avoid extremely includes the time profiles obtained for each analyte and each fiber. The best efficiencies were obtained using a desorption time of 15 min for fiber PIL-1b, while most analytes reached the equilibrium after only 5 min of desorption for the PIL-4 sorbent coating. With regard to the PA fiber, the optimum desorption time was found at 5 min for the majority of the analytes.

3.2.2. Assessment of the extraction efficiency in comparison with a commercial SPME fiber, and estimation of partition coefficients

The extraction efficiency of the studied fibers in the overall DI-SPME-HPLC-DAD method was assessed by measuring the area obtained for each analyte in a working solution of 30 $\mu\text{g}\cdot\text{L}^{-1}$ using the optimum conditions for each fiber ($n = 3$). Figure 2 (A) shows the comparison between the chromatographic peak areas obtained

using the PIL-1b, PIL-4 and PA fibers. Considering the results obtained, it can be observed that the commercial PA fiber results in a more efficient extraction of alkylphenols. However, it is important to mention that the PIL-1b fiber provided comparable results for n-NP (peak area 7.9 ± 0.6) when compared with the PA fiber (peak area 8.2 ± 1.8), and better precision, despite differences in coating thicknesses among the fibers. Regarding the nature of PIL-based sorbents coatings, PIL-1b exhibited higher peak areas for the analytes in comparison with PIL-4 fiber, except for BPA, which were similar.

Determining the partition coefficients (K_{fs}) is often the best approach to compare the extraction performance of different SPME fibers. This is particularly true considering the nature of the sorbent coating and independent of the fiber thickness. These values refer to the equilibrium that analytes experience between the sample and the sorbent phase of the fiber. The partition coefficients for the PIL-1b, PIL-4 and PA fibers were estimated using equation 1.

The calculated partition coefficients for all analytes and each fiber are included in Table 3, expressed as logarithms ($\log K_{fs}$). It is important to point out that the partition coefficients obtained are not totally quantitative values because: (1) the equilibrium conditions for each fiber are not guaranteed in the DI-SPME-HPLC method, and (2) the coating volumes for PIL-based fibers are approximate values estimated by optical microscopy. Despite these assumptions, the obtained results with partition coefficients correlate adequately with those previously observed when comparing the analytical performance of the fibers. Furthermore, partition coefficients are all obtained in the same conditions for the coatings used, and thus they are useful to establish comparisons.

According to the results contained in Table 3, it should be highlighted that the K_{fs} value using the PIL-1b fiber for all alkylphenols are higher than PA. This high affinity demonstrates that the PIL-1b fiber may be a promising sorbent coating for the extraction of these analytes, especially for n-NP. It is clear that the benzyl group in the structure of the PIL improves the π - π interactions toward these aromatic compounds. In addition, the PIL-4 fiber presents better values for BPA, which may be related to the possible hydrogen bonding interactions that enhanced its affinity for polar compounds.

3.2.3. Analytical parameters for the optimized DI-SPME-HPLC-DAD method for alkylphenols

The c DI-SPME-HPLC-DAD calibration curves were obtained for the alkylphenols with each fiber: PIL-1b, PIL-4 and PA, and several of their quality analytical parameters are included in Table 4. All calibration curves presented high correlation coefficients within the linear range studied between 0.990 and 0.999. The sensitivity of the method (assessed as the calibration slope) was higher for OP and n-NP, independent of the fiber employed. In all cases, the commercial PA fiber provided the higher calibration slopes. However, it must be pointed out that the PIL-1b coating provided satisfactory sensitivities for all analytes, with slope values not so different from the ones obtained with the PA fiber. LODs were calculated as three times the signal to noise ratio, and were validated by decreasing the analyte concentration of a standard until this ratio was achieved. The lowest LODs were achieved using the PA fiber: $2.0 \mu\text{g}\cdot\text{L}^{-1}$ for BPA, $1.0 \mu\text{g}\cdot\text{L}^{-1}$ for CuP, $0.5 \mu\text{g}\cdot\text{L}^{-1}$ for t-OP and OP, and $0.6 \mu\text{g}\cdot\text{L}^{-1}$ for n-NP. However, the PIL-4 fiber presented a value of $1.0 \mu\text{g}\cdot\text{L}^{-1}$ for BPA, demonstrating the great affinity and sensitivity previously pointed out for this PIL-based fiber toward this analyte.

The extraction efficiency of a SPME fiber may be considered depending on the chemical nature, film thickness, and surface area of the sorbent coating [39]. However, there is an important difference on the film thicknesses of the PIL-based fibers (~35 μm) and PA coating (85 μm). In these cases, several works in the literature [18,26] have proposed the utilization of the normalized calibration slopes to compare the extraction efficiency of the different coatings. This parameter is calculated as the ratio between the calibration slope obtained from the overall method and the film thickness of the fiber. Thus, the differences found on the efficiencies are only attributed to the nature of the SPME coating. This approach supports the data obtained with the estimation of partition coefficients.

Figure 2 (B) includes the normalized calibration slopes calculated for the PIL-based and PA fibers. The PIL-1b fiber is more sensitive for the entire group of phenols in comparison with the other fibers studied, excepting BPA, for which the PIL-4 fiber shows a slightly higher value. The results indicate that PIL-based sorbent coatings may be more sensitive and efficient for the extraction of this group of analytes if the film thickness of these fibers is increased at the same level as commercial fibers. In addition, the different behavior observed for both PIL-based fibers demonstrate the versatility of these novel coatings for the extraction of different compounds, which can be improved by modifying the chemical structure of the polymer.

In addition, intra- and inter-day recovery and precision studies were accomplished with all the fibers at different spiked concentration levels, as shown in Table S3 from ESM. The intra-day precision at 30 $\mu\text{g}\cdot\text{L}^{-1}$, expressed as RSD, varied from 5.4 to 16% for PIL-1b, from 6.1 to 18% for PIL-4, and from 5.7 to 19% for PA. Since the PIL-1b fiber showed comparable results to PA fiber, an intra-day precision study was carried out at lower concentration levels for both fibers. Thus, PIL-1b

presented RSD values from 11 to 15% at $10\ \mu\text{g}\cdot\text{L}^{-1}$, and from 7.2 to 15% at $20\ \mu\text{g}\cdot\text{L}^{-1}$, whereas the commercial fiber exhibited RSDs ranging from 6.1 to 16% at $10\ \mu\text{g}\cdot\text{L}^{-1}$. With regard to the PIL-based coatings, PIL-1b had the best results for most analytes. Therefore, an inter-day precision study was accomplished for this fiber at different spiked levels. The results obtained were lower or similar to the intra-day precision values achieved, with RSD ranges of 2.5-19% at $10\ \mu\text{g}\cdot\text{L}^{-1}$, 4.2-18% at $20\ \mu\text{g}\cdot\text{L}^{-1}$, and 8.2-18% at $30\ \mu\text{g}\cdot\text{L}^{-1}$. It is important to point out that the RSD values found are completely adequate, especially if the low concentration levels, the manual DI-SPME procedure, and the *off-line* desorption step are considered. Furthermore, it should be highlighted that significant differences between PIL-based fibers and PA fiber RSD values were not found.

With regard to relative recovery study (RR in %), the values obtained at the different concentration levels with each fiber were within the acceptable requirements, being higher than 70% and lower than 120%. PIL-1b had average values of 106 and 108% at $10\ \mu\text{g}\cdot\text{L}^{-1}$, 103 and 84.6% at $20\ \mu\text{g}\cdot\text{L}^{-1}$, 89.6 and 98.4 % at $30\ \mu\text{g}\cdot\text{L}^{-1}$, for the intra-day and inter-day study respectively. In the case of PIL-4, a RR average value of 82.7% was found at $30\ \mu\text{g}\cdot\text{L}^{-1}$, while PA fiber showed RRs of 111% at $10\ \mu\text{g}\cdot\text{L}^{-1}$, and 76.7% at $30\ \mu\text{g}\cdot\text{L}^{-1}$, being the lowest value reached in this study.

3.2.4. Evaluation of matrix effect and analysis of real samples

An evaluation of matrix effect for the overall DI-SPME-HPLC-DAD method was performed using tap water collected from the laboratory, which was shown to be free of analytes after being subjected to the validated method. This study was only performed using the PIL-1b fiber as a representative PIL-based coating. Table S4 from ESM includes some analytical quality parameters for the calibration curves. In comparison

with the calibration curves obtained in ultrapure water, the sensitivity (calibration slope) was higher for BPA in the water matrix. For the remaining analytes, the slopes decreased in tap water. These values go in line with the LODs obtained, which are higher than the obtained in ultrapure water for all analytes, except for BPA, which has a value of $1 \mu\text{g}\cdot\text{L}^{-1}$ in tap water.

In order to assess the presence of matrix effect, the slopes obtained in ultrapure water and tap water were statistically compared by using the Student's *t*-test reported by Andrade *et al.* [40]. In all cases, F_{ext} was lower than F_{critical} , thus both calibration slopes are assumed to be equals in view of the variance. Then, the Student's *t*-test provided t_{exp} values higher than t_{critical} for all analytes. This means that both slopes are significantly different and therefore, matrix effect must be considered.

Based on the previous results, the matrix calibration curves were employed to carry out the relative recovery and precision study to demonstrate the application of the method for the analysis of real water samples. Hence, different samples were analyzed: the tap water employed to assess matrix effect was heated and used to fill different empty plastic bottles to evaluate the migration of the analytes from the plastic (bottled water 1 and bottled water 2), and bottled water acquired from a local market (bottled water 3). Bottled water 1 and 2 were spiked at $50 \mu\text{g}\cdot\text{L}^{-1}$, while bottled water 3 was spiked at concentration level of $30 \mu\text{g}\cdot\text{L}^{-1}$. The results are included in Table S4 of ESM. RSD (intra-day precision) values were lower than 16% in all cases. It is worth mentioning that these RSD values are adequate if the experimental conditions of the method are considered. Regarding the relative recovery, all the samples provided similar values. Bottled water 1 presented an average value of 83.1%, for bottled water 2, the average RR was 89.1%, while bottled water 3 had a value of 89.5%.

4. Conclusions

Different crosslinked PILs were thoroughly evaluated in DI-SPME-HPLC-DAD for the analytical determination of a group of ten different model analytes including polar analytes such as BPA and non-polar analytes (including hydrocarbons) such as Nap. An exhaustive optimization of the whole extraction-desorption method (including the analysis of real water samples) together with a comparison of their performance with commercial SPME coatings, showed that the nature of two of the studied fibers (polymers PIL-1a and PIL-3) exert certain selectivity for the extraction of polar compounds.

PIL-1b (identical to PIL-1a but with thicker coating, $\sim 35\ \mu\text{m}$) and PIL-4 (similar to PIL-3 but containing the chloride anion to ensure higher affinity towards polar compounds, and also with a thicker coating: $\sim 35\ \mu\text{m}$), were then thoroughly evaluated in DI-SPME-HPLC-DAD; considering also the importance of obtaining coatings with thicknesses closer to that of commercial coatings. In this case, the applications was intended for the analytical determination of a group of five alkylphenols, including BPA and NP, also carrying out a deep comparison with the best commercial SPME coating to determine alkylphenols: PA, and analyzing real water samples. It was observed that the PIL-1b fiber gave average relative recoveries of 108% and inter-day precision values lower than 19% (for a spiked level of $10\ \mu\text{g}\cdot\text{L}^{-1}$). Correlations coefficients for the overall method with the PIL-1b fiber ranged between 0.990 and 0.999, and limits of detection were down to $1\ \mu\text{g}\cdot\text{L}^{-1}$ for the fiber PIL-4. Partition coefficients ($\log K_{\text{fs}}$) for the alkylphenols to the specific SPME coating varied from 1.69 to 2.45 for PIL-1, and from 1.58 to 2.30 for PA, pointing out the high affinity of the PIL-1 for the analytes studied if compared to PA. On the other side, the PIL-4

fiber presented the highest value for BPA (1.73). Furthermore, it was demonstrated that the use of normalized slopes as an adequate tool to qualitatively compare among analytical performances of SPME fibers presenting different thicknesses, with conclusions totally in agreement with that of the partition coefficients.

Crosslinked PIL solvents open the possibility of their extended use not only in GC but in HPLC, showing stability towards organic solvent such as methanol and also working at low pH values. PIL-based fibers were able to resist up to 100 extraction-desorption steps, while maintaining their structural integrity and also their analytical performance.

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Figure Captions

- Figure 1** Comparison of the extraction efficiency for each fiber when testing model analytes measured as normalized peak area, calculated as the ratio between the peak area obtained under the optimized extraction/desorption conditions described in the text, and the film thickness of each coating. Concentrations of analytes were: Cmz 200 $\mu\text{g}\cdot\text{L}^{-1}$, Bnzal 400 $\mu\text{g}\cdot\text{L}^{-1}$, BPA 400 $\mu\text{g}\cdot\text{L}^{-1}$, NP 10 $\mu\text{g}\cdot\text{L}^{-1}$, tftOL 400 $\mu\text{g}\cdot\text{L}^{-1}$, tButP 200 $\mu\text{g}\cdot\text{L}^{-1}$, EB 200 $\mu\text{g}\cdot\text{L}^{-1}$, Nap 100 $\mu\text{g}\cdot\text{L}^{-1}$, Gfz 25 $\mu\text{g}\cdot\text{L}^{-1}$, and Irg 10 $\mu\text{g}\cdot\text{L}^{-1}$.
- Figure 2** Comparison of the extraction efficiency for PIL-1b, PIL-4 and PA in the determination of alkylphenols measured as A) the peak area obtained under the optimized extraction/desorption conditions described in the text (concentration of analytes: 30 $\mu\text{g}\cdot\text{L}^{-1}$), and B) normalized calibration slopes, calculated as the ratio between the calibration slope and the film thickness of the sorbent coating.

761 **Table 1.** Chemical composition and characteristics of the cross-linked PIL-based
 762 sorbent coatings studied for HPLC.

Fiber abbreviation	IL monomer	IL cross-linker ^a	Film thickness (μm)
PIL-1a	ViBC ₁₆ Im-NTf ₂	(ViBIm) ₂ C ₁₂ -2NTf ₂	~14
PIL-1b	ViBC ₁₆ Im-NTf ₂	(ViBIm) ₂ C ₁₂ -2NTf ₂	~35
PIL-2	ViC ₁₆ Im-NTf ₂	(ViIm) ₂ C ₁₂ -2NTf ₂	~13
PIL-3	ViC ₁₆ Im-Br	(ViIm) ₂ C ₁₂ -2Br	~14
PIL-4	ViC ₆ Im-Cl	(ViIm) ₂ C ₁₂ -2Br	~35

^a 50 % (w/w) of the crosslinker in the IL monomer

763

764 **Table 2.** Quality analytical parameters for the overall DI-SPME-HPLC method using the PIL–1a, PIL–2 and PIL–3 fibers for model analytes in
765 ultrapure water.

Analyte	Fiber PIL–1a				Fiber PIL–2				Fiber PIL–3			
	Linear range ($\mu\text{g}\cdot\text{L}^{-1}$)	Slope $\pm$ SD ^a	R ^b	LOD ^c ($\mu\text{g}\cdot\text{L}^{-1}$)	Linear range ($\mu\text{g}\cdot\text{L}^{-1}$)	Slope $\pm$ SD ^a	R ^b	LOD ^c ($\mu\text{g}\cdot\text{L}^{-1}$)	Linear range ($\mu\text{g}\cdot\text{L}^{-1}$)	Slope $\pm$ SD ^a	R ^b	LOD ^c ($\mu\text{g}\cdot\text{L}^{-1}$)
Cmz	40-500	14.1 $\pm$ 0.5	0.991	20	40-500	10.3 $\pm$ 0.2	0.999	20	40-500	7.2 $\pm$ 0.1	0.999	20
Bnzal	40-500	7.7 $\pm$ 0.9	0.991	20	40-500	9.5 $\pm$ 0.1	0.999	20	40-500	7.2 $\pm$ 0.4	0.994	20
BPA	20-500	14 $\pm$ 1	0.991	10	20-500	25.8 $\pm$ 0.4	0.999	10	10-500	32.2 $\pm$ 0.2	0.999	5.0
NP	5-500	93 $\pm$ 7	0.997	2.5	10-500	13.6 $\pm$ 0.1	0.999	5.0	10-500	84 $\pm$ 1	0.999	2.5
tfTol	40-500	14 $\pm$ 2	0.990	20	40-500	9.2 $\pm$ 0.1	0.999	20	40-500	14.6 $\pm$ 0.5	0.999	20
tButP	40-500	9.1 $\pm$ 0.7	0.996	20	10-500	24.4 $\pm$ 0.4	0.999	5.0	40-500	7.7 $\pm$ 0.1	0.999	20
EB	40-500	13 $\pm$ 1	0.991	20	40-500	7.51 $\pm$ 0.03	0.999	20	40-500	12.3 $\pm$ 0.2	0.999	20
Nap	5-500	168 $\pm$ 15	0.998	2.5	10-500	72.9 $\pm$ 0.5	0.999	5.0	10-500	49 $\pm$ 1	0.999	5.0
Gfz	20-500	5.4 $\pm$ 0.4	0.995	10	20-500	21.9 $\pm$ 0.3	0.999	10	20-500	11.7 $\pm$ 0.2	0.999	10
Irg	5-500	170 $\pm$ 12	0.999	2.5	10-500	225 $\pm$ 2	0.999	2.0	5-500	172 $\pm$ 4	0.998	2.5

^a error of the slope for n = 7 calibration levels

^b correlation coefficient

^d limit of detection, calculated as three times signal to noise ratio (S/N), and verified with standards prepared at these levels and subjected to the overall method

766 **Table 3.** Estimated partition coefficients, expressed as $\log K_{fs}$, for the alkylphenols
767 studied and the PIL-1b, PIL-4 and PA fiber coatings.

$\log K_{fs} \pm \text{error}^a$			
Analyte	Fiber PIL-1b	Fiber PIL-4	Fiber PA
BPA	1.69 ± 0.06	1.73 ± 0.06	1.58 ± 0.03
CuP	2.05 ± 0.02	1.50 ± 0.08	1.83 ± 0.01
t-OP	2.45 ± 0.01	1.85 ± 0.05	2.25 ± 0.01
OP	2.39 ± 0.01	2.36 ± 0.01	2.30 ± 0.01
n-NP	2.44 ± 0.01	2.35 ± 0.01	2.05 ± 0.01

^a error in the determination of the $\log K_{fs}$, calculated from the error in the prediction of n_f and considering the mathematical propagation of errors

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769 **Table 4.** Quality analytical parameters for the overall DI-SPME-HPLC method for alkylphenols in ultrapure water using the PIL–1b, PIL–4, and
770 commercial PA fibers.

Analyte	Fiber PIL–1b				Fiber PIL–4				Fiber PA			
	Linear range ($\mu\text{g}\cdot\text{L}^{-1}$)	Slope $\pm$ SD ^a	R ^b	LOD ^c ($\mu\text{g}\cdot\text{L}^{-1}$)	Linear range ($\mu\text{g}\cdot\text{L}^{-1}$)	Slope $\pm$ SD ^a	R ^b	LOD ^c ($\mu\text{g}\cdot\text{L}^{-1}$)	Linear range ($\mu\text{g}\cdot\text{L}^{-1}$)	Slope $\pm$ SD ^a	R ^b	LOD ^c ($\mu\text{g}\cdot\text{L}^{-1}$)
BPA	10–100	115 $\pm$ 5	0.999	2.0	10–90	119 $\pm$ 11	0.996	1.0	10–100	182 $\pm$ 8	0.998	2.0
CuP	5–100	127 $\pm$ 8	0.997	2.7	10–100	35.8 $\pm$ 0.8	0.999	2.9	10–100	188 $\pm$ 20	0.990	1.0
t-OP	5–100	210 $\pm$ 9	0.999	1.7	20–90	52 $\pm$ 4	0.996	2.2	10–100	336 $\pm$ 5	0.999	0.5
OP	5–100	365 $\pm$ 18	0.998	2.4	10–90	131 $\pm$ 12	0.996	3.3	10–100	597 $\pm$ 18	0.999	0.5
n-NP	5–100	390 $\pm$ 23	0.997	2.1	10–100	124 $\pm$ 6	0.998	1.9	10–100	509 $\pm$ 40	0.994	0.6

^a error of the slope for n = 7 calibration levels

^b correlation coefficient

^d limit of detection, calculated as three times signal to noise ratio (S/N), and verified with standards prepared at these levels and subjected to the overall method

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Figure 1 - with color

Figure 1 - B&W for printing

Figure 2 - with color

Figure 2 - B&W for printing

PIL-BASED SORBENT COATINGS IN DI-SPME-HPLC-DAD FOR DETERMINING WATER POLLUTANTS

Normalized calibration slopes for alkylphenols