Determination of volatile polycyclic aromatic hydrocarbons in waters using headspace solid-phase microextraction with a benzyl-functionalized crosslinked polymeric ionic liquid coating

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\textbf{ABSTRACT}

A benzyl-functionalized crosslinked polymeric ionic liquid (PIL), produced through the co-polymerization of the 1-vinylbenzyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide (VBHDIM-NTf\textsubscript{2}) ionic liquid (IL) monomer and 1,12-di(3-vinylbenzylimidazolium)dodecane bis [(trifluoromethyl)sulfonyl]imide ((DVBIM)\textsubscript{2}C\textsubscript{12}2NTf\textsubscript{2}) IL crosslinker, was successfully used as a sorbent coating in headspace solid-phase microextraction (SPME) coupled to gas chromatography (GC) with flame-ionization detection (FID) to determine seven volatile polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. Optimum extraction conditions for the PAHs when using the novel sorbent include an extraction temperature of 50°C, an ionic strength content adjusted with 30% (w/v) NaCl in the aqueous sample, and an extraction time of 60 min. The extraction performance of the crosslinked PIL fiber was compared to the SPME commercial coating polydimethylsiloxane fiber. The calibration ranges of the studied PAHs were linear in the range of 0.02–20 µg L\textsuperscript{−1} for the crosslinked PIL fiber. The accuracy of the proposed method was demonstrated by examining the spiked recoveries of seven PAHs which produced values ranging from 67.2% to 130% (for river- and seawater samples), and precision values lower than 9.4% for a spiked level of 1 µg L\textsuperscript{−1}, and detection limits between 0.01 and 0.04 µg L\textsuperscript{−1}, which supports the sensitivity of the method using GC–FID.

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\section{1. Introduction}

Polycyclic aromatic hydrocarbons (PAHs) are mostly generated from incomplete combustion of organic compounds at high-temperature pyrolysis reactions. They have mainly a natural origin (geochemical processes), but they also have a number of sources due to transportation of vehicles, industrial wastes, and domestic heating [1]. It is well known that they can accumulate on sediments, soils, and biological organisms because of their lipophilic properties [2]. They are widely found in the atmosphere as well as in environmental water sources. Their widespread environmental presence together with their toxic and carcinogenic effects [3,4] justifies their intensive monitoring by international agencies, such as the United States Environmental Protection Agency (US-EPA), and even by the European Union (EU).

Due to the presence of PAHs at very low levels in environmental samples, sample preparation methods involving clean-up and enrichment steps are often required prior to the chromatographic analysis. The detection and monitoring of PAHs in environmental water sources often involve the use of liquid–liquid extraction or, mainly, solid-phase extraction methods [3,5]. Nowadays, microextraction procedures, with greener advantages, are preferred. Among them, liquid-phase microextraction (LPME) and solid-phase microextraction (SPME) methods can be highlighted [6,7], because they permit the minimization (in LPME) and even elimination (in SPME) of toxic organic solvents during sample preparation.

SPME is interesting because of its simplicity, speed, low cost, and high enrichment factors, particularly when compared to traditional extraction techniques. Sampling, extraction, and preconcentration steps are performed in one step by this method, and it can be easily automated. When using gas chromatography (GC), direct desorption can be performed in the injector, thus avoiding further losses of analytes. This technique has been widely used in the trace analysis of organic and biological compounds, even metals, in
environmental, food, and pharmaceutical samples [8–10]. By this technique, direct-immersion (DI) and headspace (HS) sampling analysis have been accomplished with good sensitivity and selectivity.

The sorbent coating material is highly important in SPME. Main commercial SPME materials are polydimethylsiloxane (PDMS), carboxen–PDMS, polyacrylate (PA), and divinylbenzene (DVB)–PDMS. It must be highlighted that the number of commercially available SPME coating is currently limited to seven. Novel sorbent materials, such as single- or multi-walled carbon nanotubes [11,12], polymeric ionic liquids (PILs) [13,14], and conductive polymers [15], have emerged as novel sorbent coating materials for SPME.

Crosslinked PIL-based sorbent coatings have been synthesized by UV-initiated on-fiber co-polymerization in addition to linear polymerization methods [16,17]. The crosslinked PIL-based coated fibers possess better mechanical and thermal stabilities compared to linear polymers.

The aim of this work is to compare the extraction performance of a functionalized, hydrophobic PIL-based coating possessing strong π–π interaction capabilities with a commercial PDMS fiber for the analysis of volatile PAHs in environmental samples, such as seawater and river water using HS–SPME–GC. The crosslinked PIL fiber was prepared through the UV-initiated copolymerization of the 1-vinylbenzyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl] imide (VBHDIM-NTf2) IL monomer and 1,12-di(3-vinylbenzylimidazolium)dodecane bis[(trifluoromethyl)sulfonyl] imide (DVBMI2C12-2NTf2) dicationic IL crosslinker. Furthermore, the PAH to sorbent coating partition coefficients were determined to further examine the sorption characteristics of the prepared sorbents. This study is the first to utilize a benzyl-functionalized crosslinked PIL-based sorbent coating for the extraction of PAHs from real water samples by HS–SPME.

2. Materials and methods

2.1. Chemicals and materials

The chemicals 1-vinylimidazole, hexadecyl chloride, 4-vinylbenzyl chloride (97%), 1,12-dibromododecane, vinyltrimethoxysilane (VTMS), ammonium hydrogen difluoride, and 2-hydroxy-2-methylpropiophenone (DAROCUR 1173) were purchased from Sigma-Aldrich (Milwaukee, WI, U.S.A.). Lithium bis [(trifluoromethyl)sulfonyl]imide (Li-NTf2) was supplied by SynQuest Labs (Alachua, FL, U.S.A.). The studied PAHs were supplied by Sigma-Aldrich: naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene. Hexane, methanol, acetonitrile, and sodium chloride were purchased from Fisher Scientific (Fair Lawn, NJ, U.S.A.). Ultrapure water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, U.S.A.). Seawater was obtained from the Charleston Bay (Charleston, SC, U.S.A.) and river water from the Maumee River (Maumee, OH, U.S.A.).

The homemade SPME fiber comprised untreated fused silica capillary tubing (0.5 mm I.D.) supplied by Supelco (Bellefonte, PA, U.S.A.) and a 10 µL syringe supplied by Hamilton (Reno, NV, U.S.A.). A commercial SPME fiber of PDMS, with 7 µm of film thickness, and a manual SPME holder was obtained from Supelco. Amber glass vials (20 mL) with polytetrafluoroethylene (PTFE) septa caps were also obtained from Supelco.

All studied PAH standards were dissolved individually in hexane for calibration studies in the liquid injection mode, and dissolved in acetonitrile for SPME studies. In both cases, a standard solution containing all studied PAHs of 2000 µg mL\(^{-1}\) was prepared.

An intermediate stock standard solution containing naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene was prepared at a concentration of 200 µg mL\(^{-1}\) in hexane for instrumental calibration studies. Hexane was used in the preparation of diluted working standard solutions for instrumental calibration studies. All stock solutions were stored at 4°C.

Three intermediate stock standard mixture solutions containing all PAHs in acetonitrile were prepared, at concentration values of 100, 25, and 5 µg mL\(^{-1}\), respectively. The SPME calibration working solutions were prepared by spiking a certain amount of these intermediate solutions into a saturated sodium chloride solution (30% (w/v)) with a calibration range of 0.02–20 µg L\(^{-1}\). The acetonitrile content of the aqueous solution was kept less than 0.5% (v/v) in all studies. All aqueous solutions were prepared using ultrapure water.

2.2. Instrumentation

An HP 5890 series II gas chromatograph equipped with a flame-ionization detector (FID) was used throughout this study. An HP-1 column (30 m \(\times\) 0.32 mm I.D.) supplied by Agilent Technologies (Santa Clara, CA, U.S.A.) was used. Nitrogen carrier gas with a flow rate of 1 mL min\(^{-1}\) was employed in this study. Desorption of the fibers was carried out in the splitless mode at 250°C for 5 min in all studies. The following separation temperature program was employed in the GC oven: 80°C for 2 min, then 8°C min\(^{-1}\) up to 220°C and held for 2 min, and then 25°C min\(^{-1}\) up to 300°C and held for 5 min. The temperature of the detector was set to 300°C.
The thickness of the prepared PIL fiber was measured by a JEOL JSM-7500F scanning electron microscope (SEM) from BrandX (Tokyo, Japan). An RPR-100 UV reactor employing a spinning carousel was obtained from Southern New England Ultraviolet Company (Bradford, Connecticut). The UV reactor utilized 16 lamps that produced 360 nm radiation.

2.2. Preparation of PIL-based sorbent coating and SPME fiber

The VBHDIM-NTf₂ IL monomer and (DVBIM)₂C₁₂-2NTf₂ dicationic IL crosslinker were synthesized following previously published procedures [17–20]. Chemical structures of the IL monomer and IL crosslinker used to synthesize the crosslinked PIL-based sorbent coating (which will be named as PIL–benzyl) are shown in Figure 1.

The PIL–benzyl SPME fiber was prepared according to a published procedure [16]. Briefly, a 1 cm segment of the polyimide coating was removed from the fused silica capillary tubing. The bare fiber was then immersed in a 5% (w/v) methanolic solution of ammonium hydrofluoride for 30 min, dried in air for 30 min, and conditioned in a GC injector port at 250°C for 1 h. Later, the etched fiber was immersed in 10 mL of VTMS solution for 30 min. The derivatized fiber was conditioned in the GC injection port at 200°C for 5 min. The fiber was then coated with a mixture containing the IL monomer, crosslinker (50%, w/w), and 3% (w/w) of photoinitiator. The coated fiber was then subjected to 360 nm UV light for 2 h and then conditioned 10 times at 250°C for 5 min each in the inlet of the gas chromatograph.

2.3. HS–SPME procedure

HS–SPME experiments were performed, under optimized conditions, using aqueous working solutions prepared from the aforementioned stock mixture of PAHs standard solution into 15 mL of an aqueous sodium chloride solution (30%, w/v), in a 20 mL sampling vial containing the stir bar. Extractions were performed at 50°C using a metallic block, a magnetic stirrer, and a heater. The PIL fiber was exposed to the HS of the sampling vial for 1 h (under optimized conditions) by stirring at 750 rpm. The fiber was then retracted and exposed to the GC injection port for 5 min at 250°C.

Carryover was examined after performing extractions, especially when relatively high concentrations of PAHs were tested, and it was found to be lower than 6%.

3. Results and discussion

3.1. Optimization of the HS–SPME–GC–FID method for PAHs

It is well known that main effects exerting an influence in HS–SPME are the ionic strength, the extraction temperature, the aqueous pH for ionizable analytes, and the extraction time. Thus, the effect of salt content in the initial aqueous sample, the extraction temperature, and the extraction time were investigated.

The optimization of the HS–SPME–GC–FID method for the PAHs analysis was undertaken for the benzyl fiber and for the commercial PDMS fiber, in order to have both fibers at their optimum conditions. Given the enormous influence that coating thickness exerts in SPME efficiency [21], the PDMS fiber with 7 µm thickness was selected in order to have comparable results with the PIL–benzyl fiber (~1 µm, according to the SEM measurements). The test solutions were prepared using 15 mL of an aqueous standard mixture of PAHs at 10 µg L⁻¹. The stirring velocity and other fixed conditions are detailed in the experimental section.

The solubility of many organic compounds decrease by the addition of salt to the aqueous solution due to the well-known salting out effect, thus, forcing the increasing presence of volatile compounds in the HS. Aqueous solutions with the NaCl content varying from 0 to 30% (w/v) at room temperature (25°C) for PIL–benzyl fiber, and at 40°C for PDMS fiber were studied. Amounts of NaCl higher than 30% (w/v) were not studied to avoid precipitation as the solubility of NaCl in water is ~30 g/100 mL at 25°C: roughly 30% (w/v). Furthermore, the NaCl content of 30% (w/v) is also comparable to that of many seawaters. As shown in Figure S1A (supplemental material), the addition of salt resulted in an increase in the extraction efficiency for all studied PAHs, especially for naphthalene, acenaphthene, and fluorene using the PIL–benzyl fiber. Similar results were obtained for the PDMS fiber, as shown in Figure S1B.
(supplemental material). The best results were obtained at 30% (w/v) NaCl for both fibers. Indeed, the extraction efficiency was two to five times higher when using 30% of NaCl (w/w) than the efficiencies obtained when no salt was added. This content was therefore selected in the remaining experiments.

The extraction efficiency for the HS analysis is also highly influenced by the extraction temperature. By increasing the extraction temperature, a greater content of analytes in the HS can result in higher analyte enrichment. However, caution must be also taken because the sorption process on the fiber is endothermic. The effect of temperature on the extraction efficiency of each PAH was studied by varying the extraction temperature from 24°C to 60°C for 30 min. For the PIL–benzyl fiber, it was observed that the extraction efficiency for all analytes at 60°C was nearly threefold higher than that obtained at room temperature, as shown in Figure S2A (supplemental material). For comparison purposes, the extraction temperature was also optimized for the PDMS fiber using extraction temperatures of 24°C, 40°C, 50°C, and 60°C, and an extraction time of 30 min without the addition of salt. As shown in Figure S2B (supplemental material), the extraction efficiency of PAHs increased at 40°C but then decreased above this temperature. Hence, extraction temperatures of 50°C for the PIL–benzyl fiber and 40°C for the PDMS fiber were chosen for subsequent experiments.

Finally, the extraction time of the HS–SPME–GC–FID method was optimized from 15 to 120 min. Longer times were not tested to avoid a tedious methodology. The sorption time profiles obtained for each PAH are shown in Figure S3A and S3B (supplemental material) for the PIL–benzyl and PDMS fibers, respectively. The extraction efficiencies of the studied PAHs for both fibers reached the maximum at 60 min and slightly decreased at longer times for most PAHs. Therefore, a 60 min extraction time was chosen for all subsequent experiments as a compromise solution.

### 3.2. Estimation of partition coefficients

Under optimum conditions, it is of enormous importance to quantify the strength of the affinity between the studied PAHs and both fibers. The obtained partition coefficient values are an accurate comparison tool among sorbent materials.

It can be conceived that the partitioning of the analytes between the sample solution and the SPME fiber is determined by the partition coefficient ($K_{fs}$). In HS–SPME, the partitioning of the analyte takes place initially from the sample to HS, followed by the HS to fiber during extraction. The partition coefficients used for these equilibria are expressed as $K_{gs}$ and $K_{fg}$, respectively. By considering equilibrium conditions and ideal gas behavior for the studied analytes, the analyte amount extracted by the fiber ($n_f$) can be determined using the following equation [22]:

$$n_f = \frac{K_{fg} c_0 V_f}{K_{gs} V_f + K_{gs} V_g + V_s}, \tag{1}$$

where $K_{fs}$ is the partition coefficient of the analyte between the sample and the coating of fiber ($K_{fs} = K_{gs} \times K_{fg}$); $c_0$ is the is the initial concentration of the analyte in the sample (in ng mL$^{-1}$); $V_g$, $V_s$, and $V_f$ are, respectively, the volumes of the gas phase (HS), the sample, and the coating of fiber.

Generally, it is known that $K_{gs}$ values of volatile analytes are comparatively small [23]. Additionally, Equation (1) can be simplified by considering the volume of fiber much lower than the volume of sample ($V_f \ll V_s$), becoming as:

$$n_f = K_{fs} c_0 V_f, \tag{2}$$

Thus, the estimation of $K_{fs}$ can be easily calculated using Equation (2) for the volatile analytes. It must be emphasized that the $K_{fs}$ values calculated with these considerations are not absolute values of partition coefficients and are only estimates.

The determination of partition coefficients was conducted using an initial PAH concentration of 1 µg L$^{-1}$ in the aqueous sample. The volume of the commercial PDMS fiber coating was 0.0260 µL, as reported by the manufacturer. The film thickness of the PIL–benzyl fiber was estimated as 1 µm, which is similar to the value obtained for the same fiber (2 µm) in another study [17]. The SEM image of the PIL–benzyl fiber is shown in Figure 2. The film thicknesses of the fibers produced by crosslinked co-polymerization are sometimes thinner than the noncrosslinked PIL fibers synthesized through thermal polymerization methods using azobisisobutyronitrile initiation [13,17,23]. The coating volume of the PIL–benzyl fiber was calculated using the cylindrical layer of polymer on the fused silica support having a diameter of 140 µm and 1 cm length. Thus, the volume of the PIL fiber was estimated as 0.0044 µL.

The $n_f$ values were obtained through the amount of analyte extracted by the fibers compared with the direct injection method using an initial concentration of $c_0$. The estimated partition coefficients are given in Table 1. It must be noted that the $K_{fs}$ values obtained in this study are only approximate values because we are not working under equilibration conditions. In addition, the $n_f$ values have been estimated by an external calibration method (Table S1) (supplemental material). Besides, the estimated volume of the PIL-
based coating is only an approximation. However, the results are completely valid to evaluate new crosslinked, co-polymeric PILs-based materials as SPME coatings because all partition coefficients ($K_{fs}$) are calculated using the same conditions.

In all cases, higher log $K_{fs}$ values for the crosslinked PIL fiber coating were obtained compared to the PDMS fiber coating for the PAHs, indicating the superior affinity of the PIL fiber. Higher partition coefficients for the PIL–benzyl coating may be due to the presence of benzyl moieties within the IL monomer and IL crosslinker of the crosslinked PIL sorbent coating, which enhances $\pi$–$\pi$ interactions between the analytes and the sorbent coating. Log $K_{fs}$ values for PAHs with the PIL–benzyl fiber range from 5.65 to 6.24 when using HS–SPME. These values are higher than those obtained when utilizing the noncrosslinked poly(1-4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl] imide (poly-VBHDIM-NTf$_2$) coating, which ranged from 3.30 to 5.04 in the Di-SPME mode [13]. That polymer was synthesized by thermal polymerization [13]. Both fibers have benzyl moieties in IL monomer, but the crosslinker within the PIL–benzyl fiber has additional benzyl moieties which may further enhance $\pi$–$\pi$ interactions.

3.3. Analytical performance of the HS–SPME–GC–FID method for PAHs determination

Once the overall HS–SPME–GC–FID method was optimized and the effectiveness of the PIL coatings was demonstrated by the high partition coefficient values obtained. It is important to evaluate the performance of the method to clearly point out its advantages over commercial fibers. The figures of merit of the proposed method, including the linear range, precision, correlation coefficient of the calibration curves, sensitivities and limits of detection (LOD) for PIL–benzyl, and PDMS fibers were obtained and are shown in Tables 2 and 3, respectively.

The linearity of the PIL–benzyl fiber and PDMS fiber was tested up to 20 µg L$^{-1}$ of PAHs. The linear range varied between 0.02 and 20 µg L$^{-1}$ for the PIL–benzyl fiber with correlation coefficients higher than 0.997 and between 0.03 and 20 µg L$^{-1}$ for the PDMS fiber, with correlation coefficients higher than 0.996.

Sensitivities of all PAHs evaluated through the slopes of the calibration curves were much higher with the PIL–benzyl fiber than those obtained with the PDMS fiber, practically twice or even higher.

The LODs were estimated as three times the standard deviation at the lowest concentration on the calibration curve, divided by the slope of the calibration curve. The obtained LODs for the PIL–benzyl fiber were better than for the PDMS fiber. They ranged from 0.01 to 0.04 µg L$^{-1}$ for the PIL–benzyl fiber and from 0.01 to 0.07 µg L$^{-1}$ for the PDMS fiber. This is significant, particularly considering that the PDMS fiber is almost seven times thicker than the PIL–benzyl fiber. The maximum allowable concentration of some PAHs in environmental waters are recommended as 130 µg L$^{-1}$ for naphthalene,
0.1 µg L\(^{-1}\) for anthracene, and 0.12 µg L\(^{-1}\) for fluoranthene by the EU [24]. It is clear that these values can be detected using the proposed method.

Precision was determined by performing three extractions at a low concentration of PAHs in deionized water: 1 µg L\(^{-1}\). The relative standard deviation (RSD) values (in %) for the PIL–benzyl fiber and PDMS fiber varied from 2.8% to 7.9% and from 1.0% to 9.0%, respectively, pointing out the intraday precision obtained at low spiked levels.

A comparison between the crosslinked PIL sorbent coating to other homemade coatings and commercial materials used in HS–SPME–GC with regard to linear ranges, precision, and LODs is summarized in Table 4. It can be observed that the performance of the proposed method is totally adequate, including high sensitivity despite the utilization of GC–FID. Thus, detection limits are comparable and even lower than those obtained with other polymer-based materials for HS–SPME when using GC–FID [25,26]. It is clear that if combined the PIL-based coatings developed in this work with GC–MS, much better sensitivity would be obtained. Regarding precision, it was tested in this work using a low spiked level of 1 µg L\(^{-1}\), whereas others reports utilized 2 µg L\(^{-1}\) [25], and 10 µg L\(^{-1}\) [26] for GC–FID. Once again, low spiked levels can be tested for our PIL materials if GC–MS is used instead of GC–FID. In any case, the RSD values are always lower than 7.9%, which is totally adequate, and lower than other values reported, such as 13% [26,30].

Table 2. Figures of merit of the HS–SPME–GC–FID calibration curves for the PIL–benzyl fiber.

| PAH            | Calibration range (µg L\(^{-1}\)) | Slope ± SD \(^{(a)}\) | Intercept ± SD \(^{(a)}\) | \(\delta^2\) | R\(^{(c)}\) | LOD\(^{(d)}\) (µg L\(^{-1}\)) | RSD\(^{(e)}\) (%) |
|----------------|----------------------------------|-----------------------|-------------------------|-------------|-------------|-----------------------------|------------------|
| Naphthalene    | 0.05–20                          | 1.93 ± 0.04           | 0.61 ± 0.32             | 0.69        | 0.999       | 0.02                        | 3.8              |
| Acenaphthene   | 0.10–20                          | 4.09 ± 0.11           | 2.93 ± 0.93             | 1.98        | 0.998       | 0.04                        | 3.3              |
| Fluorene       | 0.02–20                          | 4.37 ± 0.13           | 1.68 ± 1.11             | 2.39        | 0.998       | 0.01                        | 2.8              |
| Phenanthrene   | 0.10–20                          | 7.64 ± 0.08           | 0.67 ± 0.67             | 1.51        | 0.999       | 0.01                        | 7.9              |
| Anthracene     | 0.10–20                          | 6.19 ± 0.10           | 0.86 ± 0.83             | 1.86        | 0.999       | 0.01                        | 5.4              |
| Fluoranthene   | 0.10–20                          | 3.73 ± 0.09           | 1.35 ± 0.78             | 1.75        | 0.998       | 0.01                        | 7.9              |
| Pyrene         | 0.10–10                          | 2.20 ± 0.08           | 0.86 ± 0.33             | 0.73        | 0.997       | 0.02                        | 7.2              |

\(^{(a)}\) Standard deviation of the slope and the intercept, for \(n=7\) calibration levels.

\(^{(b)}\) Standard deviation of regression (or error of the estimate).

\(^{(c)}\) Coefficient of correlation.

\(^{(d)}\) Estimated as three times the standard deviation at the lowest concentration on the calibration curve, divided by the slope of the calibration curve.

\(^{(e)}\) Based on three extractions, intraday precision (as RSD in %), using an aqueous standard containing 1 µg L\(^{-1}\) for all PAHs.

Table 3. Figures of merit of the HS–SPME–GC–FID calibration curves for the PDMS fiber (7 µm).

| PAH            | Calibration range (µg L\(^{-1}\)) | Slope ± SD \(^{(a)}\) | Intercept ± SD \(^{(a)}\) | \(\delta^2\) | R\(^{(c)}\) | LOD\(^{(d)}\) (µg L\(^{-1}\)) | RSD\(^{(e)}\) (%) |
|----------------|----------------------------------|-----------------------|-------------------------|-------------|-------------|-----------------------------|------------------|
| Naphthalene    | 0.15–10                          | 0.46 ± 0.02           | 0.31 ± 0.08             | 0.17        | 0.996       | 0.07                        | 8.8              |
| Acenaphthene   | 0.15–20                          | 2.00 ± 0.07           | 0.32 ± 0.62             | 1.32        | 0.997       | 0.06                        | 9.0              |
| Fluorene       | 0.03–20                          | 1.78 ± 0.03           | 0.95 ± 0.23             | 0.49        | 0.999       | 0.01                        | 7.3              |
| Phenanthrene   | 0.15–20                          | 1.87 ± 0.04           | 1.74 ± 0.38             | 0.83        | 0.999       | 0.02                        | 7.2              |
| Anthracene     | 0.10–10                          | 2.22 ± 0.09           | 1.86 ± 0.40             | 0.82        | 0.999       | 0.04                        | 1.9              |
| Fluoranthene   | 0.20–10                          | 2.05 ± 0.08           | 1.30 ± 0.36             | 0.75        | 0.996       | 0.03                        | 4.4              |
| Pyrene         | 0.25–10                          | 2.62 ± 0.06           | 1.06 ± 0.26             | 0.53        | 0.999       | 0.04                        | 2.5              |

\(^{(a)}\) Standard deviation of the slope and the intercept, for \(n=7\) calibration levels.

\(^{(b)}\) Standard deviation of regression (or error of the estimate).

\(^{(c)}\) Coefficient of correlation.

\(^{(d)}\) Estimated as three times the standard deviation at the lowest concentration on the calibration curve, divided by the slope of the calibration curve.

\(^{(e)}\) Based on three extractions, intraday precision (as RSD in %), using an aqueous standard containing 1 µg L\(^{-1}\) for all PAHs.

Table 4. A comparison between different SPME materials for the determination of PAHs in water samples.

| Type of sorbent          | Method      | Linear range (µg L\(^{-1}\)) | LOD (µg L\(^{-1}\)) | Precision (RSD%)/Spiked level used for obtaining the precision is written in parenthesis Ref. |
|--------------------------|-------------|------------------------------|--------------------|--------------------------------------------------|
| Poly(3,4-ethylenedioxythiophene)/graphene oxide composite | CF\(^{(a)}\)–HS–SPME–GC–FID | 0.4–600 | 0.05–0.13 | 4.8–8.4/(2 µg L\(^{-1}\)) [25] |
| PDMS–DVB                 | MA\(^{(b)}\)–HS–SPME–GC–FID | 0.1–200 | 0.03–1.0 | 5–13/(10 µg L\(^{-1}\)) [26] |
| Periodic mesoporous organosilica–ionic liquid frame network | HS–SPME–GC–MS | 0.05–10 | 0.004–0.009 | 4.3–9.7/(5 µg L\(^{-1}\)) [27] |
| Ethoxylated nonylphenol coating | HS–SPME–GC–MS | 0.05–200 | 0.01–0.5 | 4.9–8.4/(0.5 µg L\(^{-1}\)) [28] |
| Graphene                 | HS–SPME–GC–MS | 0.005–0.5 | 0.001–0.003 | 4.9–9.3/(0.1 µg L\(^{-1}\)) [29] |
| Aniline–silica nanocomposite | HS–SPME–GC–MS | 0.02–4 | 0.001–0.003 | 6–13/(40 ng L\(^{-1}\)) [30] |
| PIL–benzyl               | HS–SPME–GC–FID | 0.01–20 | 0.01–0.04 | 2.8–7.9/(1 µg L\(^{-1}\)) This work |

\(^{(a)}\) CF, cold fiber.

\(^{(b)}\) MA, microwave assisted.
Table 5. Relative recovery and precision obtained with the HS–SPME–GC–FID method when using the PIL–benzyl and PDMS fibers with real samples (river water and seawater), spiked at low levels of PAHs.

| PAH          | PIL–benzyl fiber | PDMS (7 µm) fiber |
|--------------|-----------------|-----------------|
|              | River water*    | Seawater*       | River water*    | Seawater*       |
|              | Found (µg L⁻¹) | RR (%) | RSD (%) | Found (µg L⁻¹) | RR (%) | RSD (%) | Found (µg L⁻¹) | RR (%) | RSD (%) |
| Naphthalene  | 1.030           | 103     | 1.2    | 1.300         | 130    | 2.2     | 1.160         | 116    | 4.1     |
| Acenaphthene | 0.992           | 99.2    | 5.4    | 0.991         | 99.1   | 5.4     | 1.130         | 113    | 9.4     |
| Fluorene     | 0.999           | 99.9    | 6.2    | 0.672         | 67.2   | 3.5     | 1.030         | 103    | 3.9     |
| Phenanthrene | 0.978           | 97.8    | 2.4    | 0.807         | 80.7   | 3.8     | 0.831         | 83.1   | 9.4     |
| Anthracene   | 1.040           | 104     | 2.2    | 0.842         | 84.2   | 3.7     | 0.747         | 74.7   | 4.6     |
| Fluoranthene | 1.000           | 100     | 7.3    | 0.740         | 74.0   | 3.5     | 1.030         | 103    | 3.9     |
| Pyrene       | 1.110           | 111     | 9.4    | 0.767         | 76.7   | 7.4     | 0.905         | 90.5   | 4.6     |

*Relative recovery and intraday precision (n = 3) for a spiked level of 1 µg L⁻¹ of PAHs.

3.4. Application to the analysis of real water samples

To evaluate the performance of the proposed method for the extraction of PAHs by HS–SPME–GC–FID with real complex samples, river- and seawater were employed. Prior to recovery and precision studies, both river and seawater samples were analyzed and proved to be free of PAHs (or, at least, with contents below the LOD of the method). Three replicate analyses were performed by spiking 1 µg L⁻¹ of the PAHs in the water sample, and the HS–SPME–GC–FID method was carried out under optimized conditions for each fiber. The obtained results are given in Table 5. Relative recoveries range from 97.8% to 111% for river water using the PIL–benzyl fiber, from 67.2% to 130% for seawater using the PIL–benzyl fiber, from 74.7% to 116% for river water using the PDMS fiber, and from 77.0% to 110% for seawater using the PDMS fiber. RSD values were lower than 9.4% in all cases, which highlights the reproducibility of the method. No obvious damage to the fibers was observed during the analysis, which was indicative of the long lifetime of the coating materials.

4. Conclusions

In this study, a crosslinked PIL–benzyl fiber was successfully applied for the HS–SPME extraction of PAHs coupled with GC–FID for two different real water samples. The analytical performance of the crosslinked PIL fiber in the HS extraction of PAHs was comparably better than the commercial PDMS fiber and a similar non-crosslinked PIL coating produced by linear polymerization in spite of its lower film thickness. The LODs for PAHs were found in the range of part per trillion in the aqueous salty solution at elevated temperatures using GC–FID. It is clear that the combined use of GC–MS would increase enormously the sensitivity of the method.

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Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1] Ke Y, Zhu F, Jiang R, et al. Determination of polycyclic aromatic hydrocarbons in leather products using solid-phase microextraction coupled with gas chromatography-mass spectrometry. Microchem J. 2012;111:159–163.
[2] Liguori L, Heggstad K, Hove HT, et al. An automated extraction approach for isolation of 24 polyaromatic hydrocarbons from various marine matrixes. Anal Chim Acta. 2006;573–574:181–188.
[3] Titato GM, Lancas FM. Comparison between different extraction (LLE and SPE) and determination (HPLC and capillary-LC) techniques in the analysis of selected PAHs in water samples. J Liq Chromatogr Related Technol. 2005;28:3045–3056.
[4] Zhang K, Zhang BZ, Li SM, et al. Calculated respiratory exposure to indoor size-fractioned polycyclic aromatic hydrocarbons in an urban environment. Sci Total Environ. 2012;431:245–251.
[5] Liu X, Lu X, Huang Y, et al. Fe₃O₄@ionic liquid@methyl orange nanoparticles as a novel nano-adsorbent for magnetic solid-phase extraction of polycyclic aromatic hydrocarbons in environmental water samples. Talanta. 2014;2005;8:3045–3056.
[6] Sanagi MM, Loh SH, Ibrahim WAW, et al. Agarose film liquid phase microextraction combined with gas chromatography-mass spectrometry for the determination of polycyclic aromatic hydrocarbons in water. J Chromatogr A. 2012;1262:43–48.
[7] Dias AN, Simao V, Merib J, et al. Cork as a new green coating for solid-phase microextraction: determination of polycyclic aromatic hydrocarbons in water samples by gas chromatography-mass spectrometry. Anal Chim Acta. 2013;772:33–39.
[8] Bianchin JN, Nardini G, Merib J, et al. Screening of volatile compounds in honey using a new sampling strategy...
combining multiple extraction temperatures in a single assay by HS-SPME-GC-MS. Food Chem. 2014;145:1061–1065.

[9] Michulec M, Wardencki W. Development of headspace solid-phase microextraction-gas chromatography method for the determination of solvent residues in edible oils and pharmaceuticals. J Chromatogr A. 2005;1071:119–124.

[10] Shahdousti P, Alizadeh N. Headspace-solid phase micro-extraction of selenium(IV) from human blood and water samples using polypyrrole film and analysis with ion mobility spectrometry. Anal Chim Acta. 2011;684:67–71.

[11] Li Q, Wang X, Yuan D. Preparation of solid-phase microextraction fiber coated with single-walled carbon nanotubes by electrophoretic deposition and its application in extracting phenols from aqueous samples. J Chromatogr A. 2009;1216:1305–1311.

[12] Liu H, Li J, Liu X, et al. A novel multiwalled carbon nanotubes bonded fused-silica fiber for solid phase microextraction-gas chromatographic analysis of phenols in water samples. Talanta. 2009;78:929–935.

[13] Meng Y, Anderson JL. Tuning the selectivity of polymeric ionic liquid sorbent coatings for the extraction of polycyclic aromatic hydrocarbons using solid-phase microextraction. J Chromatogr A. 2010;1217:6143–6152.

[14] Pang L, Liu JF. Development of a solid-phase microextraction fiber by chemical binding of polymeric ionic liquid on a silica coated stainless steel wire. J Chromatogr A. 2012;1230:8–14.

[15] Tamer U, Ertas N, Udum YA, et al. Electrochemically controlled solid-phase microextraction (EC-SPME) based on overoxidized sulfonated polypyrrole. Talanta. 2005;67:245–251.

[16] Ho TD, Yu H, Cole WTS, et al. Ultraviolet photoinitiated on-fiber copolymerization of ionic liquid sorbent coatings for headspace and direct immersion solid-phase microextraction. Anal Chem. 2012;84:9520–9528.

[17] Joshi MD, Ho TD, Cole WTS, et al. Determination of polychlorinated biphenyls in ocean water and bovine milk using crosslinked polymeric ionic liquid sorbent coatings by solid-phase microextraction. Talanta. 2014;118:172–179.

[18] Zhao F, Meng Y, Anderson JL. Polymeric ionic liquids as selective coatings for the extraction of esters using solid-phase microextraction. J Chromatogr A. 2008;1208:1–9.

[19] Anderson JL, Ding RF, Ellem A, et al. Structure and properties of high stability geminal dicaticonic ionic liquids. J Am Chem Soc. 2005;127:593–604.

[20] Anderson JL, Armstrong DW. Immobilized ionic liquids as high-selectivity/high-temperature/high-stability gas chromatography stationary phases. Anal Chem. 2005;77:6453–6462.

[21] Alpendurada MD. Solid-phase microextraction: a promising technique for sample preparation in environmental analysis. J Chromatogr A. 2000;889:3–14.

[22] Zhang Z, Pawliszyn J. Headspace solid-phase microextraction. Anal Chem. 1993;65:1843–1852.

[23] Trujillo-Rodriguez MJ, Yu H, Cole WTS, et al. Polymeric ionic liquid coatings versus commercial solid-phase microextraction coatings for the determination of volatile compounds in cheeses. Talanta. 2014;121:153–162.

[24] European Commission, Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Offic J Eur Union. 2013; L 226/1.

[25] Banitaba MH, Davarani SSH, Movahed SK. Comparison of direct, headspace and headspace cold fiber modes in solid phase microextraction of polycyclic aromatic hydrocarbons by a new coating based on poly(3,4-ethylenedioxythiophene)/graphene oxide composite. J Chromatogr A. 2014;1325:23–30.

[26] Wei MC, Jen JF. Determination of polycyclic aromatic hydrocarbons in aqueous samples by microwave assisted headspace solid-phase microextraction and gas chromatography/flame ionization detection. Talanta. 2007;72:1269–1274.

[27] Abolghasemi MM, Karimi B, Yousefi V. Periodic mesoporous organosilica with ionic liquid framework as a novel fiber coating for headspace solid-phase microextraction of polycyclic aromatic hydrocarbons. Anal Chim Acta. 2013;804:286.

[28] Es-haghi A, Hosseinzadeh V, Bagheri H. Preparation, characterization, and applications of a novel solid-phase microextraction fiber by sol-gel technology on the surface of stainless steel wire for determination of polycyclic aromatic hydrocarbons in aquatic environmental samples. Anal Chim Acta. 2014;813:48–55.

[29] Zhang S, Du Z, Li G. Layer-by-layer fabrication of chemically bonded graphene coating for solid-phase microextraction. Anal Chem. 2011;83:7531–7541.

[30] Bagheri H, Roostaie A. Aniline-silica nanocomposite as a novel solid phase microextraction fiber coating. J Chromatogr A. 2012;1238:22–29.