Ionic liquid-based graphene oxide-coated fiber for headspace-solid phase microextraction of polycyclic aromatic hydrocarbons in water samples

Pelin ERDEM[1] , **Paniz TASHAKKORI**[2] , **Melek MERDİVAN**[1] , **Serap SEYHAN BOZKURT**[1,*]

[1]Department of Chemistry, Faculty of Science, Dokuz Eylül University, İzmir, Turkey
[2]Graduate School of Natural and Applied Science, Dokuz Eylül University, İzmir, Turkey

Abstract: Ionic liquid (IL) containing amino and vinyl terminated imidazolium cation and bis[(trifluoromethyl)sulfonyl] imide anion-functionalized graphene oxide (GO) coating material was prepared and coated on a stainless steel wire by a sol-gel technique for headspace-solid phase microextraction (HS-SPME). Its extraction performance was checked by HS-SPME of polycyclic aromatic hydrocarbons (PAHs) coupled to gas chromatography with mass spectrometry (GC-MS). The extraction capability of the IL-functionalized GO-coated fiber was comparable with that of the commercial fibers of polydimethylsiloxane (PDMS) and polydimethylsiloxane/carboxen/divinylbenzene (PDMS/CAR/DVB). Under the optimized conditions, such as extraction temperature, extraction time, and salting-out, the proposed HS-SPME-GC-MS method presented a wide working range from 0.003 to 40 μg L^{-1} with a correlation coefficient higher than 0.996, low detection limits from 1 to 5 ng L^{-1}, and good precision less than 7%. The fiber-to-fiber repeatability was in the range of 0.2%–6.9%. The recoveries for 8 PAHs using the novel and commercial fibers in tap and seawater samples were obtained very close to each other and were in the range of 75.4% to 116.0%.

Key words: Graphene oxide, ionic liquid, SPME, GC-MS, PAH, sol-gel, water samples

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed of two or more aromatic rings and appear in the environment during the pyrolysis of hydrocarbons at high temperatures. They are widely present as pollutants in the atmosphere as well as in water and have carcinogenic and toxic effects for human health and the environment. They are found in the atmosphere as well as in environmental water sources since petroleum, coal, hookah smoke, and industrial smoke are common sources of them. The presence of very small amounts of these substances in tap water may cause toxic and carcinogenic effects in the human body [1]. In nature over 100 PAH compounds are present because of incomplete combustion of coal, gas, rubbish, tobacco, etc. However, only 16 of these are considered by the US Environmental Protection Agency (EPA) as priority pollutants [2]. The maximum residue limit of PAHs for the level of the most carcinogenic benzo[α]pyrene in drinking water established by the EPA is 0.2 μg L^{-1} for human consumption [3]. The sample preparation methods involving clean-up and enrichment steps are often required before the chromatographic analysis of PAHs at subtrace levels in environmental samples. The detection of PAHs in environmental water sources usually involves the use of solid-phase extraction [4], stir bar sorptive extraction [5], dispersive liquid–liquid microextraction [6], and solid

---

*Correspondence: serap.seyhan@deu.edu.tr

phase microextraction (SPME) coupled to gas chromatography (GC) or high-performance liquid chromatography (HPLC) [7,8]. These extraction techniques have advantages such as speed, low cost, high enrichment factor, and high recovery. However, SPME has been preferred because of its shorter analysis time and no requirement for a clean-up step [9].

SPME is an equilibrium extraction procedure that is applied by a coated fiber to extract organic compounds from the analytical matrices by direct-immersion or headspace technique. Headspace-SPME is based on the interaction between the vapor phase of the sample and the fiber. In this mode, the fiber is not inserted into the sample solution and so the fiber coating is protected from direct contact with the matrix, which can cause contamination of the fiber surface. Compounds in the vapor phase of the sample reach the surface of the fiber coating by diffusion or natural airflow [7]. In direct-immersion mode, the fiber is immersed in the sample solution during extraction [8]. In addition, more volatile and hydrophobic compounds are preconcentrated at the headspace of the sample and the extraction of semivolatile and polar compounds is accomplished by direct-immersion mode. Following this, the separation and determination of retained compounds are generally carried out by GC or HPLC. This technique is fast, simple, solvent-free, and suitable for automation [9]. One of the most important parameters in SPME is the choice of sorbent material to be coated on the fiber. It is required to fabricate new fibers with a fixed substrate and selective coating towards the target analytes in order to obtain high extraction efficiency due to the extraction requirement of different trace environmental pollutants [10]. Silica [11,12], chitosan [13], and graphene oxide [14] have been widely employed as coating materials for SPME fibers. Graphene oxide has been used in analytical sample preparation due to its large surface area, high affinity towards particularly aromatic hydrocarbons, high adsorption capacity, and good mechanical properties. Because of the presence of oxygenated groups in GO, different functionalized GO materials have been prepared and utilized in different extraction techniques [15]. Its selectivity towards organic molecules has been remarkably increased by linking with ionic liquids [16].

Ionic liquids have physical properties such as high thermal stability, low volatility, low vapor pressure, high ionic conductivity, and high miscibility with solvents. Different functional sorbents have been combined with ILs by surface modification due to their superior physicochemical properties. These sorbents have been used in separation and enrichment methods such as solid phase extraction and solid phase microextraction [17,18]. They also ensure that the extraction methods are environmentally friendly.

In the present work, graphene oxide modified with 1-(3-aminopropyl)-3-vinyl imidazolium bis [(trifluoromethyl)sulfonyl]imide $[\text{H}_2\text{N-C}_3\text{vim}^+][\text{TFSI}^-]$ was prepared, coated on a stainless steel wire by sol-gel technique, and utilized for determination of 8 PAHs chosen as model compounds in aqueous samples at trace level by HS-SPME-GC-MS. The aim was that the presence of hydrophobic ionic liquid would cause an increase in the thermal stability of the coating material on the fiber and the selectivity towards the organic analytes. Extraction temperature, extraction time, and salting-out as experimental parameters affecting the extraction efficiency were optimized. The extraction performance of the prepared fiber was compared with that of commercial SPME fibers (PDMS and PDMS/CAR/DVB) and the proposed method was applied to the analysis of eight PAHs in real water samples.

2. Results and discussion

2.1. Characteristics of IL-functionalized GO and the surface of GO-[H_2N-C_3vim^+][$TFSI^-$]-coated fiber

The FTIR spectra of GO and IL-functionalized GO are given in Figure 1a. The FTIR spectrum of GO showed a broad and intense O–H stretching vibration at 3310 cm^{-1}. Two absorption peaks at 1719 cm^{-1} and 1610 cm^{-1} are due to the stretching vibration of C=O and C=C groups in the aromatic parts. The peaks at 1410, 1265, and 1032 cm^{-1} correspond to the stretching vibration of the carbon skeleton and C–O of epoxy and alkoxy groups, respectively [19,20]. In the FTIR spectrum of GO-[H_2N-C_3vim^+][$TFSI^-$], the stretching vibrations of C–H in the imidazole ring, vinyl, and aliphatic groups were observed at 3108, 2967, and 2844 cm^{-1}, respectively. The peaks at 1569 and 1451 cm^{-1} corresponding to C–N and C=N vibrations indicate the presence of an imidazole ring in GO. Further, the peak at 1159 cm^{-1} corresponds to ring in-plane asymmetric stretching from the imidazolium ring and (N)CH_2 and (N)CH_3 stretching. The peaks around 820–710 cm^{-1} correspond to ring in-plane bending vibrations of C–H and (N)CH_2 and (N)CH_3 [21,22]. These results proved that ionic liquid is covalently bonded to graphene oxide.

The XRD patterns of GO and IL-functionalized GO are given in Figure 1b. The diffraction peak of graphene oxide at $2\theta = 29.92°$ corresponds to the (002) diffraction crystalline plane. The intensity of this peak depends on the degree of oxidation [23]. The diffraction peaks between 30° and 45°, especially at $2\theta = 39.5$ and 40.5°, were based on the ionic liquid crystal structure and proved the preparation of GO-functionalized material [24].

Thermal properties of IL, GO, and functionalized GO coating material were only studied up to 450 °C because the novel SPME fiber was thermally desorbed at 250 °C in the GC injection port. As shown in Figure 1c, the weight loss in GO initially started and reached approximately 10% up to 100 °C, stayed stable at 180 °C, and then gradually decreased to 65% until 450 °C. These losses are seen because of the water evaporation, and the decomposition of functional groups containing oxygen, respectively. The decomposition of the synthesized IL began at around 175 °C and the weight loss reached approximately 20%–25% at 450 °C. As a result, GO-[H_2N-C_3vim^+][$TFSI^-$] material showed better thermal stability than GO because of the presence of this ionic liquid. The residual oxygenated groups and decomposition/deformation of the surface of GO attached to IL caused weight loss above 200 °C at a lower degree with respect to GO [20]. This result showed that this coating material was suitable for the SPME method coupled to GC.

The SEM images of the GO, GO functionalized with IL, and IL-functionalized GO-coated fiber are given in Figure 1d. As seen in Figure 1d1, the SEM image of GO shows a wrinkled scaly structure. After ILs were introduced into GO, the SEM image of GO-[H_2N-C_3vim^+][$TFSI^-$] also showed a wrinkled and folded lamellar structure (Figure 1d2). The prepared fiber was imaged after about 100 sorption/desorption cycles (Figure 1d3). The coating thickness of IL-functionalized GO fiber was determined by SEM and was between 12 and 15 μm.

2.2. Optimization of the SPME method for PAHs

To achieve high extraction efficiency using the prepared GO-[H_2N-C_3vim^+][$TFSI^-$]-coated fiber several parameters including extraction mode, extraction temperature, extraction time, and salting-out were optimized. For this, the extraction was realized with different temperatures, times, and salt concentrations and the extraction efficiency was determined after each extraction for eight PAHs. The maximum extraction efficiency for each parameter was considered the optimum value.
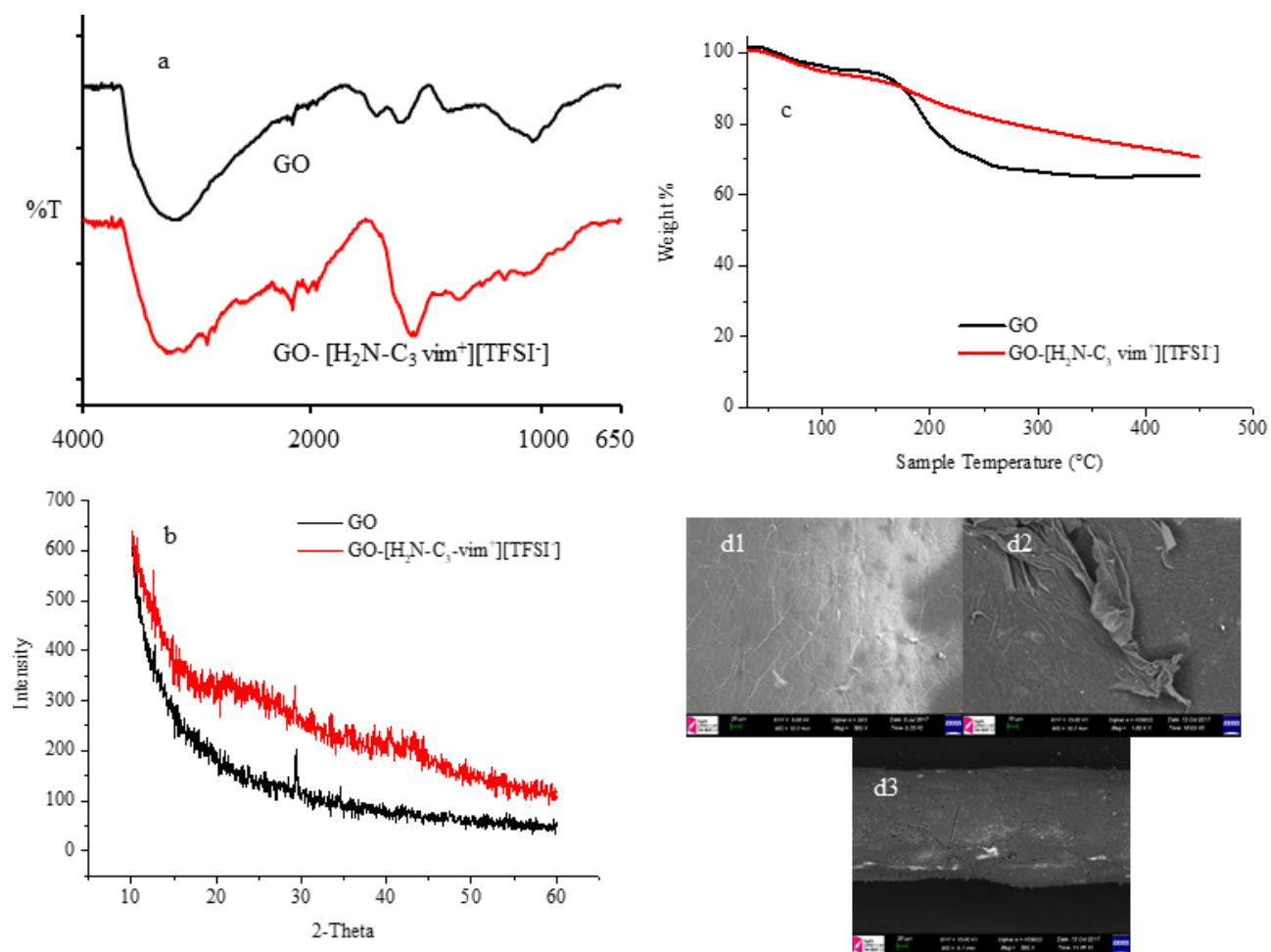
Figure 1. FTIR spectra of GO and GO-$[H_2N-C_3vim^+][TFSI^-]$ (a); XRD patterns of GO and GO-$[H_2N-C_3vim^+][TFSI^-]$ (b); thermogravimetric analysis of GO and GO-$[H_2N-C_3vim^+][TFSI^-]$ (c), SEM images of GO at $500\times$ (d1), GO-$[H_2N-C_3vim^+][TFSI^-]$ at $500\times$ (d2), and GO-$[H_2N-C_3vim^+][TFSI^-]$-coated fiber at $500\times$ magnification (d3).

2.2.1. Extraction mode

In the optimization of the SPME method, both SPME modes, headspace and direct immersion (DI), were compared using homemade SPME fiber for eight PAHs of low molecular weight. As seen in Figure 2, higher extraction efficiencies were obtained with the HS mode. Furthermore, the use of headspace is preferred to direct immersion as the compounds have poor water solubility and good volatility. Volatile and light hydrophobic compounds like PAHs are more easily transported to HS than more hydrophilic and less volatile compounds [25]. Consequently, further optimization conditions were studied in HS mode.

2.2.2. Extraction temperature

Extraction temperature is an important parameter that influences extraction efficiency because it affects the transportation of analytes from aqueous solution to HS and then to the fiber coating. In order to determine the optimum extraction temperature, the HS-SPME method was carried out from 25 to 75 °C (Figure 3a). It was seen that the extraction efficiencies of PAHs were increased by increasing the extraction temperature up to 60
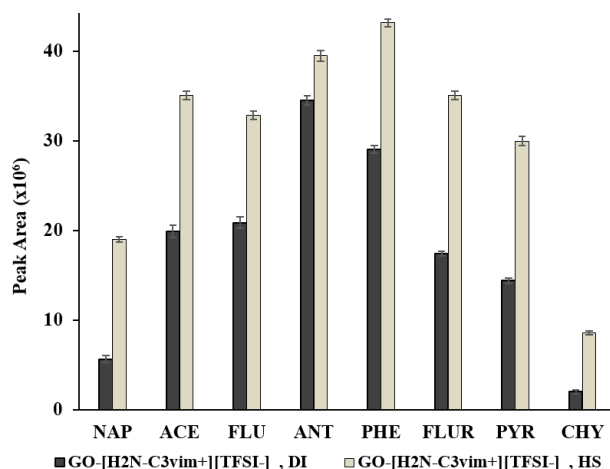
Figure 2. Effect of extraction mode in the extraction efficiency of GO-[H_2N-C$_3$vim$^+$][TFSI$^-$]-coated fiber. Conditions: C_{PAH}, 10 μg L^{-1}; extraction time, 30 min and extraction T, 50 °C, for DI; extraction time, 15 min and extraction T, 60 °C for HS.

°C, but above this temperature a decrease in efficiency was observed. This result can be explained by first the kinetic effect of high temperature for mass transfer from the aqueous phase through the fiber coating and later the thermodynamic effect of high temperature for decreasing partition coefficients in the exothermic adsorption system [25]. Thus, the optimal extraction temperature was chosen as 60 °C for further investigations.
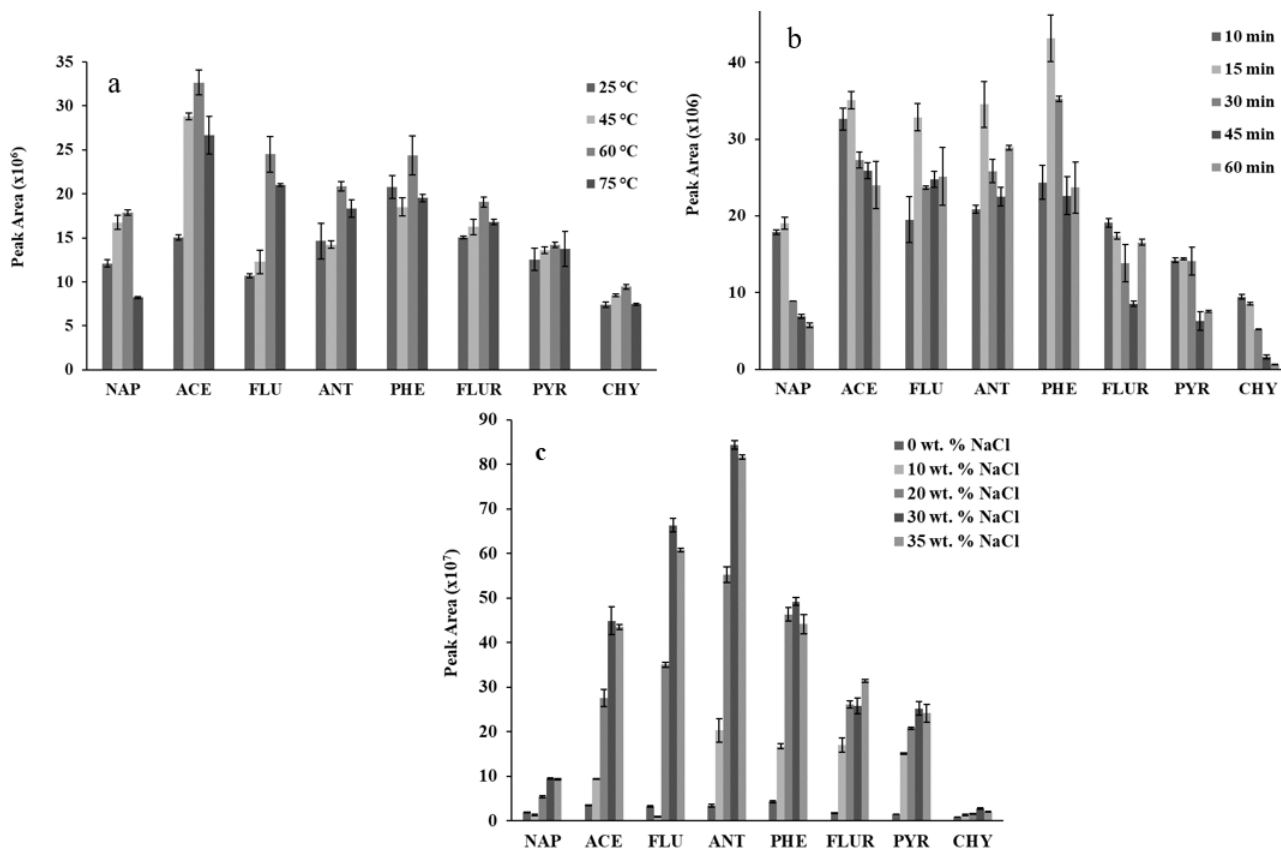

Figure 3. Effect of extraction temperature (a), extraction time (b), and NaCl concentration (c) on the extraction efficiency of GO-[H_2N-C$_3$vim$^+$][TFSI$^-$]-coated fiber, (n = 3). Conditions: C_{PAH}, 10 μg L^{-1}.

2.2.3. Extraction time

The maximum amount of analyte must be extracted on the SPME fiber at the extraction time. Therefore, the optimization of extraction time is another important parameter affecting extraction efficiency. The effect of extraction time was investigated in the range of 10–60 min and the results are given in Figure 3b. The peak areas of PAHs were increased up to 15 min and then decreased slightly at 30 min and became stable up to 60 min. This showed that PAHs could be extracted from the aqueous phase to IL-functionalized GO-coated fiber in a short time and the equilibrium was reached quickly. This fast equilibration can be explained partially by the film thickness and coating material. The thinner film thickness of GO-$[H_2N-C_3vim^+][TFSI^-]$ fiber (12–15 μm) can ensure shorter analysis time than PDMS fiber and DVB/CAR/PDMS fiber. The $TFSI^-$ anion enhanced the hydrophobicity of IL-functionalized GO and the vinyl group in the $H_2N-C_3vim^+$ cation caused an increase in the $\pi-\pi$ interaction with PAHs [26]. Thus, the extraction time was selected as 15 min for the subsequent studies.

2.2.4. Salt concentration

Ionic strength affects the solubility of organic analytes in an aqueous solution because of the salting-out effect. The salt effect on extraction was investigated by adding various concentrations of NaCl (0–35 wt.%) in 15 mL of water containing PAHs at 10 μg L^{-1} at the optimized extraction temperature and time. It was seen that the peak areas of all studied PAHs increased with the concentration of NaCl up to 30 wt.% and then decreased with the concentration of NaCl at 35 wt.% (Figure 3c) Thereby, the subsequent extractions were carried out with 30 wt. % NaCl solution.

2.3. Comparison of GO-$[H_2N-C_3vim^+][TFSI^-]$-coated fiber with sol-gel-coated fiber, GO-coated fiber, and commercial fibers

The GO-$[H_2N-C_3vim^+][TFSI^-]$-coated fiber was compared with only sol-gel-coated fiber and only GO-coated fiber for the HS-SPME method of PAHs. As shown in Figure 4, the extraction efficiency of the proposed fiber was considerably higher than that of the sol-gel-coated and GO-coated fibers.

The extraction efficiency of the GO-$[H_2N-C_3vim^+][TFSI^-]$-coated fiber was compared with that of commercial fibers (PDMS and PDMS/CAR/DVB). The HS-SPME method was also realized with commercial fibers for optimization of extraction conditions. The best NaCl concentration was determined likewise as 30 wt.% and the highest extraction efficiency was obtained above 60 °C for both commercial fibers. The extraction performances of those commercial fibers were checked at 10, 15, 30, 45, and 60 min to determine the optimum extraction time. In the optimization experiments, the equilibrium was reached at 45 min and 60 min with PDMS fiber and DVB/CAR/PDMS fiber, respectively, for PAHs. In the comparison of the extraction performances of GO-$[H_2N-C_3vim^+][TFSI^-]$-coated fiber and commercial fibers, the HS-SPME method was performed for 10 μg L^{-1} PAHs at the optimized conditions. As seen in Figure 5, GO-$[H_2N-C_3vim^+][TFSI^-]$ fiber exhibited a higher extraction efficiency for the PAHs than the PDMS and DVB/CAR/PDMS fibers due to the enhanced $\pi-\pi$ interaction with the vinyl group and imidazolium ring of the IL besides GO. Moreover, faster extraction was provided by IL-functionalized GO-coated fiber than by the PDMS and the PDMS/CAR/DVB commercial fibers.
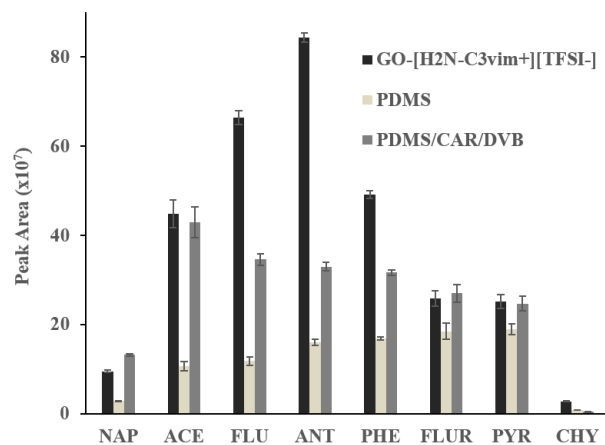
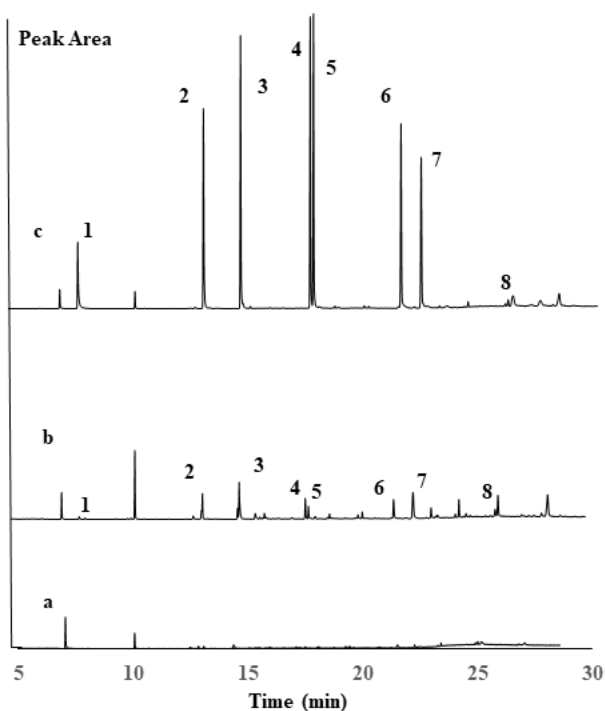**Figure 4**. Extraction ability of GO-[H$_2$N-C$_3$vim$^+$][TFSI$^-$]-coated fiber and the commercial fibers.

Figure 5. Comparison of representative chromatograms for PAHs after HS-SPME using (a) sol-gel-coated fiber, (c) GO-coated fiber, and (c) GO-[H$_2$N-C$_3$vim$^+$][TFSI$^-$]-coated fiber.

2.4. Method validation

The analytical performance of the proposed HS-SPME method with the prepared IL-functionalized GO fiber for PAHs was evaluated under the optimized conditions. Analytical parameters including linear ranges, correlation coefficients, limits of detection (LODs), single fiber repeatability, and fiber-to-fiber reproducibility were determined for each PAH (Table 1). The LODs were calculated by decreasing the concentration of analyte a little lower than that of the lowest calibration level until obtaining three times the signal to noise ratio. The linearity was tested up to 50 μg L^{-1} of each studied PAH. The linear ranges varied from 0.003 to 40 μg L^{-1} with correlation coefficients ranging from 0.996 to 0.999. For the commercial fibers, the linear ranges varied between 0.05 and 40 μg L^{-1} and the LODs were in the range of 0.01–0.05 μg L^{-1} (Table 1). The precision (as relative standard deviation (RSD)) of the proposed method was determined by three repetitions of each concentration used to constitute the calibration curve for each PAH by the single fiber. The RSD values ranged from 0.2% to 6.9%, which were lower than those obtained with the commercial fibers (PDMS, PDMS/CAR/DVB). The reproducibility of the proposed method was checked using three different fibers prepared in the same process and the RSDs were in the range of 1.4%–5.5%. Furthermore, the extraction/desorption cycle was carried out for more than 100 cycles with no considerable loss in extraction efficiencies by the IL-functionalized GO fiber. As a result, it could be concluded that the homemade SPME fiber exhibited long lifetimes with this IL-functionalized GO coating.

Table 1. Analytical parameters for HS-SPME using GO-[H2N-C3vim$^+$][TFSI$^-$] -coated fiber and commercial fibers.

Analyte	GO-[H$_2$N-C$_3$vim$^+$][TFSI$^-$] – coated fiber				PDMS- coated fiber		DVB/CAR/PDMS-coated fiber					
	Linear range (μg L^{-1})	R^b	LOD (μg L^{-1})	RSD^c (%)	Linear range (μg L^{-1})	R	LOD (μg L^{-1})	RSD (%)	Linear range (μg L^{-1})	R	LOD (μg L^{-1})	RSD (%)
NAP	0.01–40	0.998	0.005	0.2–1.5	0.1–40	0.996	0.05	1.4–5.9	0.05–40	0.998	0.01	1.0–6.4
ACE	0.01–40	0.999	0.005	0.7–1.6	0.1–40	0.996	0.05	1.7–5.6	0.05–40	0.999	0.01	1.3–7.2
FLU	0.01–40	0.997	0.005	0.6–1.6	0.1–40	0.997	0.05	133–6.0	0.05–40	0.996	0.01	1.4–8.1
ANT	0.003–40	0.996	0.001	0.4–4.2	0.05–40	0.995	0.01	1.3–6.9	0.05–40	0.996	0.01	1.8–4.7
PHE	0.003–40	0.997	0.001	1.2–6.9	0.05–40	0.995	0.01	1.9–5.9	0.05–40	0.995	0.01	1.4–5.8
FLUR	0.003–40	0.998	0.001	0.7–4.9	0.05–40	0.996	0.01	2.5–6.5	0.05–40	0.997	0.01	2.1–6.8
PYR	0.003–40	0.999	0.001	0.4–5.0	0.05–40	0.998	0.01	1.4–6.7	0.05–40	0.998	0.01	2.1–6.8
CHY	0.01–40	0.997	0.005	0.4–5.0	0.1–40	0.995	0.05	1.1–5.9	0.05–40	0.999	0.01	1.5–5.3

^{a} Error of the slope for n = 10 calibration levels.
^{b} Correlation coefficient.
^{c} Based on five extractions within a day precision.

2.5. Sample analysis

The proposed HS-SPME method was applied to the determination of eight PAH compounds in seawater and tap water using the IL-functionalized GO-coated fiber and the commercials fibers. The PAHs studied were not detected in the tap or seawater samples. The accuracy of the proposed method was examined by spiking real water samples with 1 and 5 μg L^{-1} PAH mix standard solution. Typical chromatograms of tap and sea waters achieved after the HS-SPME method are shown in Figures 6 and 7. The recoveries were in the range of 75.8%–116.0% by IL-functionalized GO-coated fiber and 75.4%–114.0% by commercial fibers for the studied PAH analytes (Table 2). The results showed that reliable quantification results were acquired for analysis of PAHs in real samples using the proposed HS-SPME method with the prepared GO-[H$_2$N-C$_3$vim$^+$][TFSI$^-$]-coated fiber.

2.6. Comparison with other SPME methods for PAHs

The developed HS-SPME-GC-MS method with IL-functionalized GO-based fiber for the determination of PAHs was compared with other SPME methods with respect to linear range, LOD, recovery, and extraction time. As seen in Table 3, linear range and LODs of the proposed method were similar or better than the reported ones. The results showed that the proposed IL-functionalized GO fiber was capable of competing with SPME fibers coated with different materials, especially poly-IL-based GO coating [27], for the determination of PAH
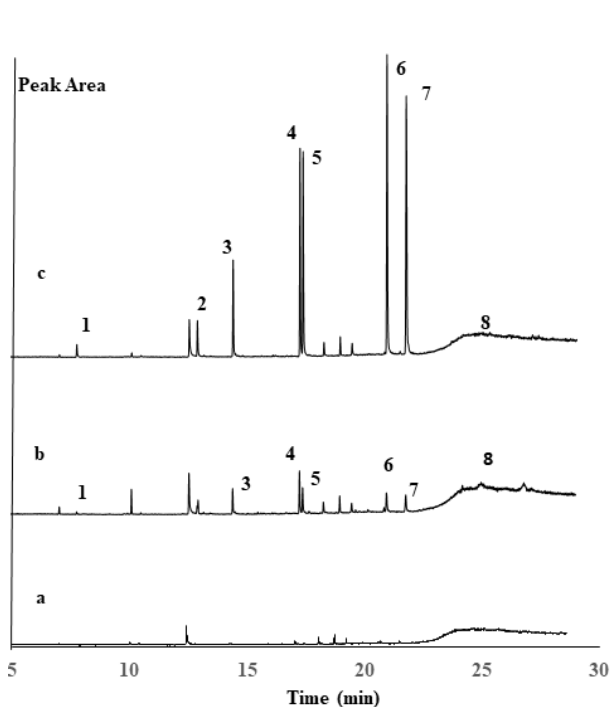
Figure 6. Chromatograms of extracts of PAHs (1; NAP, 2; ACE, 3; FLU, 4; ANT, 5; PHE, 6; FLUR, 7; PYR, 8; CHY) from (a) blank tap water sample, (b) tap water spiked at 1 μg L^{-1}, (c) tap water spiked at 5 μg L^{-1} PAHs standard solution using GO-[H$_2$N-C$_3$vim$^+$][TFSI$^-$]-coated fiber.
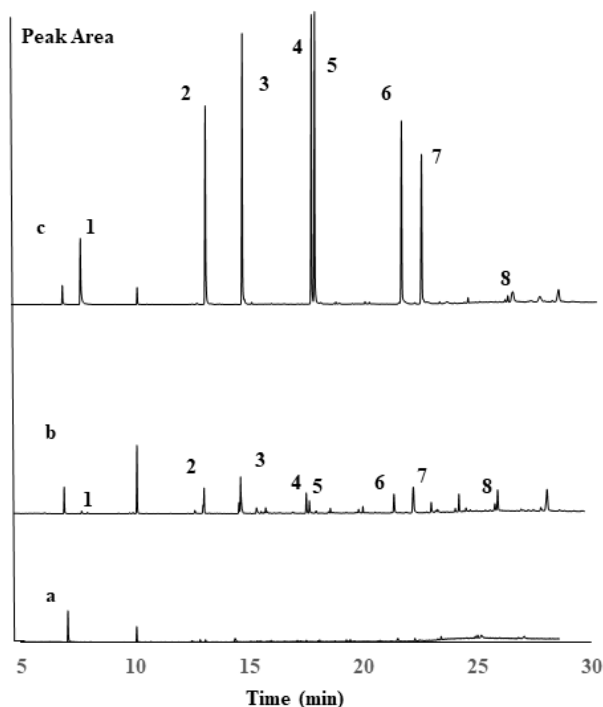
Figure 7. Chromatograms of extracts of PAHs (1; NAP, 2; ACE, 3; FLU, 4; ANT, 5; PHE, 6; FLUR, 7; PYR, 8; CHY) from (a) blank seawater sample, (b) seawater spiked 1 μg L^{-1}, and (c) seawater spiked 5 μg L^{-1} PAHs standard solution using GO-[H$_2$N-C$_3$vim$^+$][TFSI$^-$]-coated fiber.

compounds. Besides the demonstrated wide linear ranges and low LODs, the extraction time obtained with the vinyl-terminated imidazolium cation and bis[(trifluoromethyl)sulfonyl]imide anion-functionalized GO-coated fiber is much shorter than the other reported ones.

2.7. Conclusions

The IL-functionalized GO, GO-[H$_2$N-C$_3$vim$^+$][TFSI$^-$], has been used as SPME coating material to extract PAHs. The GO-IL coating was designed to have a TFSI$^-$ anion of hydrophobic character and a vinyl terminated imidazolium cation enhancing π-electrons and was able to provide van der Waals and $\pi-\pi$ interactions with PAH compounds. Under optimized experimental conditions, this fiber demonstrated wide linear ranges, low LODs, and good recoveries for water samples. The prepared IL-functionalized GO coating has a long lifetime, high thermal stability, and good repeatability and reproducibility. The GO-[H$_2$N-C$_3$vim$^+$][TFSI$^-$] fiber showed faster adsorption behavior than the PDMS and PDMS/CAR/DVB commercial fibers.

3. Experimental

3.1. Chemicals and materials

The reagents 1-vinyl imidazole, 3-bromopropylamine hydrobromide, bis(trifluoromethane) sulfonimide lithium salt (LiTFSI), tetraethylorthosilicate, polydimethylsiloxane hydroxy-terminated, N,N-dimethylformamide (DMF), trifluoroacetic acid (TFA), acetonitrile, graphene oxide (2 mg/mL), and naphthalene (NAP), phenanthrene

Table 2. Relative recovery and intraday precision of PAHs in water samples (n = 3).

| PAH | Added (μg L^{-1}) | GO-[H$_2$N-C$_3$vim$^+$][TFSI$^-$] | | | | PDMS | | | | DVB/CAR/PDMS | | | |
| | | Sea water | | Tap water | | Sea water | | Tap water | | Sea water | | Tap water | |
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
NAP	1	95.4	5.9	80.0	1.1	106	3.9	107	1.9	107	3.4	96.5	3.6
	5	98.0	1.3	94.4	3.1	101	2.5	107	10.8	93.9	1.7	85.9	5.0
ACE	1	89.7	3.8	92.5	2.4	94.4	3.9	92.1	6.7	102	9.5	106	4.1
	5	95.4	1.4	93.8	3.3	96.7	2.7	95.3	8.7	98.3	9.5	102	2.4
FLU	1	97.5	3.0	106	1.8	111	3.3	102	5.3	89.1	9.7	104	2.4
	5	95.0	2.2	75.7	1.8	103	2.4	80.3	6.2	110	2.9	102	1.0
ANT	1	87.8	3.8	85.2	2.8	90.2	6.1	87.6	9.6	94.2	6.6	93.7	0.4
	5	98.8	5.5	98.5	3.4	92.2	3.3	94.7	3.2	92.6	7.3	84.3	6.8
PHE	1	104	6.4	103	2.5	88.2	6.1	103	1.1	111	5.2	101	3.5
	5	101	6.4	90.4	1.5	96.3	9.2	80.3	1.4	92.8	2.4	86.7	1.1
FLUR	1	111	10.1	99.1	3.3	100	7.9	102	7.4	108	3.9	106	2.2
	5	103	0.9	104	3.8	86.9	5.1	103	4.1	112	3.7	100	10.5
PYR	1	80.2	2.3	79.4	3.6	100	8.6	110	6.3	81.8	6.6	88.6	2.6
	5	84.5	14.8	83.5	1.6	84.5	11.0	101	1.4	101	3.2	102	2.2
CHY	1	92.0	1.7	97.7	8.0	101	10.7	110	1.8	95.2	3.9	90.0	2.3
	5	95.2	7.3	87.4	3.7	81.4	11.2	94.4	4.4	101	1.2	103	9.1

(PHE), and chrysene (CHR) (analytical standard grade) were purchased from Sigma-Aldrich (Switzerland). Ethanol, methanol, and ethyl acetate were purchased from Merck (Germany). Acenaphthene (ACE), fluorene (FLU), anthracene (ANT), fluoranthene (FLUR), and pyrene (PYR) (analytical standard grade), polydimethylsiloxane (PDMS, 7-μm thickness) and polydimethylsiloxane/carboxen/divinylbenzene (PDMS/CAR/DVB, 50/30-μm thickness) fibers, a manual SPME holder, and transparent amber glass vials (20 mL) with polytetrafluoroethylene (PTFE)/silicone septum and caps were obtained from Supelco (USA). The commercial fibers were preconditioned before use according to the manufacturer's recommendation (1 h at 250 °C). The stainless steel wire (O.D., 0.15 mm) was supplied from a local market (Turkey) and 5-μL microsyringes used to assemble the homemade SPME device were obtained from Hamilton (USA).

A stock solution of each PAH standard as 5000 mg L^{-1} was prepared in acetonitrile. An intermediate stock solution including all studied PAHs was prepared weekly from the stock solution of each PAH at 10 μg L^{-1} with acetonitrile and used to prepare diluted working solutions with ultrapure water obtained from a Milli-Q water purification system (USA). Seawater was collected from the Urla coast of the Aegean Sea at İzmir (Turkey). Tap water was collected from Dokuz Eylül University, Chemistry Department laboratory (Turkey). Seawater samples were stored in amber glass bottles at 4 °C in darkness before use.

Table 3. Comparison with other sampling methods for the determination of PAHs.

Fiber coating & detection system	Matrix	Extraction time (min)	Linear range (μg L^{-1})	LOD (μg L^{-1})	Recovery (%)	Ref.
Graphene-HS-SPME-GC-MS	Water and soil samples	40	0.005–0.5	0.002–0.003	72–102	[32]
(OH)$_{12}$Q[6]/PDMS-HS-SPME-GC-FID	Water samples	40	0.1–1000	0.03–0.15	90.2–109.5	[7]
Home-made PDMS-HS-SPME-GC-MS	Leather samples	60	0.1–50	0.01–0.12	81.7–124.9	[33]
Ethoxylated nonylphenol-HS-SPME-GC-MS	Water samples	25	0.05–200	0.01–0.5	79–104	[34]
GO/PDMS-DI-SPME-GC-FID	Water samples	50	0.05–200	0.005–0.08	84.5–118.2	[35]
TiO$_2$/NiO@MPS-Ph-SPME-HPLC-UV	Water samples	35	0.02–500	0.004–0.005	89.4–102	[36]
Poly(VHIm$^+$NTf$_2^-$)-GO-HS-SPME-GC-FID	Potato peel samples	40	0.05–50	0.015–0.025	78.3–101.7	[16]
PoPD-co-PoT/MCNTs	Water samples	60	0.01–100	0.001–0.006	88.3–102.5	[37]
GO-[H$_2$N-C$_3$vim$^+$][TFSI$^-$]-HS-SPME-GC-MS	Water samples	15	0.003–40	0.001–0.005	75.7–115.9	This work

3.2. Instrumentation

A Thermo Fisher Scientific (USA) QP2010 GC-MS with a single quadrupole mass spectrometer detector was used. A TG-5MS capillary column (30.0 m × 0.25 mm I.D., film thickness 0.25 μm) was supplied by Thermo Scientific (USA). Ultrapure helium was used as the carrier gas, at a flow rate of 1.2 mL min^{-1}. The injector port temperature was set to 250 °C for desorption of fibers under splitless mode with 5-min sampling time in all studies. The following temperature program was applied to separate the PAHs. The GC oven was initially held at 80 °C for 2 min, then increased to 220 °C at a rate of 8 °C min^{-1} for 2 min, and then further increased to 250 °C at a rate of 15 °C min^{-1} and held for 5 min [27]. The MS ion source and interface temperatures were set to 250 °C and 280 °C, respectively. Detection of PAHs was carried out using the total-ion chromatogram (TIC) mode (full-scan 50 to 650 m/z) at a scan rate of 0.2 scans per second in the developing method. The retention times (min) obtained for the PAHs studied were 7.73 for NAP, 12.76 for ACE, 14.25 for FLU, 17.04 for ANT, 17.17 for FLUR, 20.68 for PHE, 21.48 for PYR, and 25.23 for CHR.

Fourier transform infrared (FTIR) spectra were obtained using a Thermo Scientific Nicolet iS10 model FTIR spectrometer (USA) with an attenuated total reflectance accessory in the range of 4000–650 cm^{-1}. Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy was performed on a Varian Mercury Plus-400 model NMR

spectrometer (USA). Thermal properties were investigated by PerkinElmer Diamond model thermogravime-try/differential thermal analyzer (USA) under a nitrogen atmosphere by heating from room temperature to 450 °C at 10 °C min^{-1}. Scanning electron microscopy (SEM) images were obtained using a Carl Zeiss 300 VP model (Germany) scanning electron microscope at 5 kV acceleration voltage. All X-ray diffractometer (XRD) measurements were made by a Philips X'Pert PROBE model (USA) with a monochromatic Cu-Kα X-ray source with a voltage of 40 kV and current of 30 mA at 2θ s^{-1} from 10° to 60°.

3.3. Synthesis of ionic liquids

The ionic liquid, $[H_2N\text{-}C_3vim^+][TFSI^-]$, was synthesized according to the method given in the literature [28]. Firstly, 1-vinyl imidazole was refluxed with 3-bromopropylamine in ethanol at 80 °C for 24 h under nitrogen atmosphere. The resulting product, (1-(3-aminopropyl)-3-vinyl imidazolium bromide $[H_2N\text{-}C_3vim^+][Br^-]$, was crystallized by cold ethyl acetate and dried in a vacuum oven at 60 °C overnight prior to use. Then, for the preparation of IL, $[H_2N\text{-}C_3vim^+][Br^-]$ was mixed with LiTFSI in methanol and stirred at room temperature for 24 h. Then the product was separated from the methanol phase and washed several times with deionized water until the aqueous part was free from bromide. Finally, $[H_2N\text{-}C_3vim^+][TFSI^-]$ was dried in a vacuum oven at 60 °C for 3 days for complete removal of water. It was characterized by FTIR and ^{1}H NMR; $[H_2N\text{-}C_3vim^+][TFSI^-]$ FTIR (cm^{-1}): $\nu_{N-H} = 3382$, $\nu_{=C-H} = 3149$, $\nu_{C-H} = 2957\text{–}2842$, $\nu_{C=N} = 1571$, $\nu_{C=C} = 1554$, $\nu_{C-F} = 1451$, $\nu_{C-N} = 1185$, $\nu_{C-C} = 1131$, $\nu_{S=O} = 1054$, $\nu_{C-S} = 741$. ^{1}H NMR (CD$_3$OH) δ: 7.92 (s, 1H), 7.51 (d, 1H), 7.28 (d, 1H), 5.95 (d, 2H), 5.36 (t, 1H), 4.63 (t, 2H), 3.01–2.97 (m, 2H), 2.48 (p, 2H), 1.34 (broad s, 2H).

3.4. Preparation of GO-$[H_2N\text{-}C_3vim^+][TFSI^-]$ coating material

First 10 mL of homogeneous and transparent GO dispersion in water (0.5 mg mL^{-1}) was mixed with 10 mg of $[H_2N\text{-}C_3vim^+][TFSI^-]$. To this turbid mixture was added 10 mg of KOH followed by homogenization at room temperature for 30 min using an ultrasonicator. After this epoxide ring-opening reaction, a homogeneous solution was obtained and strongly stirred at 80 °C for 24 h. The obtained GO-$[H_2N\text{-}C_3vim^+][TFSI^-]$ material was centrifuged, washed with ethanol and distilled water, and it was dried in a vacuum oven at 60 °C overnight [29].

3.5. Preparation of GO-$[H_2N\text{-}C_3vim^+][TFSI^-]$-based SPME fiber

Firstly, 1.5 cm bare wire tip of stainless steel wire was washed with acetone, ethanol, and water to remove contaminants. For etching, 1 cm tip of stainless steel wire was immersed in aqua regia:water (1:1, v/v) solution for 30 min and dried at room temperature. Secondly, the surface of a stainless steel wire was modified by OH groups. For this, 1.0 cm of the etched steel wire end was firstly washed with distilled water and dried in a desiccator at room temperature. Then it was dipped into 2 mol L^{-1} NaOH overnight and rinsed with water and dried under a nitrogen atmosphere. The outer surface of the modified stainless steel wire was left in 0.01 mol L^{-1} HCl solution for 30 min [30]. By the sol-gel coating technique, 2 mg of GO-$[H_2N\text{-}C_3vim^+][TFSI^-]$ was homogeneously dispersed using 100 μL of DMF in a 1.5-mL microcentrifuge tube and the tube was sonicated for 2 h. Then 350 μL of TEOS and 50 μL of PDMS were added to this mixture and it was sonicated for 20 min again. Finally, 50 μL of TFA (95%, v/v) solution was added followed by stirring for 5 min [31]. Finally,

the modified stainless steel wire end was vertically dipped into the prepared sol-gel composite for 1 h and dried at room temperature for 20 min. To get the desired thickness of the prepared fiber (≈ 10–12 μm), the coating process was repeated several times. Later, the coated fiber was dried at room temperature for 24 h and conditioned 6 times at 250 °C for 5 min in the injection port of the GC.

3.6. HS-SPME procedure

For the extraction of PAHs in aqueous solution, HS-SPME experiments were carried out in a 20-mL sampling vial containing 15 mL of working standard solution spiked at ten different concentrations of PAHs in the range of 0.001–50 μg L^{-1} or a sample solution. Extractions were realized at optimized conditions with a fiber using a metallic block and a heater at a constant stirring rate of 750 rpm. After extraction, the IL-functionalized GO-coated fiber was retracted into the needle and then inserted into the GC injection port for 5 min at 250 °C for desorption of PAHs. After each analysis, the fiber was subjected to a second empty GC injector for 5 min at 250 °C to eliminate carry-over effects. All experiments were carried out in triplicate.

References

1. Abdel-Shafy HI, Mansour MSM. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egyptian Journal of Petroleum 2016; 25 (1): 107-123. doi: 10.1016/j.ejpe.2015.03.011

2. Guidance for Reporting Toxic Chemicals: Polycyclic Aromatic Compounds Category. United States Environmental Protection Agency 2001; EPA 260-B-01-03.

3. Zelinkova Z, Wenzl T. The occurrence of 16 EPA PAHs in food - a review. Polycyclic Aromatic Compounds 2015; 35 (1-2): 248-284. doi: 10.1080/10406638.2014.918550

4. Xue SW, Tang MQ, Xu L, Shi ZG. Magnetic nanoparticles with hydrophobicity and hydrophilicity for solid phase extraction of polycyclic aromatic hydrocarbons from environmental water samples. Journal of Chromatography A 2015; 1411: 9-16. doi: 10.1016/j.chroma.2015.07.104

5. Bourdat-Deschamps B, Daudin JJ, Barriuso E. An experimental design approach to optimise the determination of polycyclic aromatic hydrocarbons from rainfall water using stir bar sorptive extraction and high performance liquid chromatography-fluorescence detection. Journal of Chromatography A 2007; 1167 (2): 143-153. doi: 10.1016/j.chroma.2007.08.025

6. Avino P, Notardonato I, Perugini L, Russo MV. New protocol based on high-volume sampling followed by DLLME-GC-IT/MS for determining PAHs at ultra-trace levels in surface water samples. Microchemical Journal 2017; 133: 251-257. doi: 10.1016/j.microc.2017.03.052

7. Dong N, Li T, Luo YJ, Shao L, Tao Z et al. A solid-phase microextraction coating of sol-gel-derived perhydroxy cucurbit[6]uril and its application on to the determination of polycyclic aromatic hydrocarbon. Journal of Chromatography A 2016; 1470: 9-18. doi: 10.1016/j.chroma.2016.09.066

8. Pacheco-Fernandez I, Najafi A, Pino V, Anderson JL, Avala JH et al. 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. Talanta 2016; 158: 125-133. doi: 10.1016/j.talanta.2016.05.041

9. Prosen H, Zupancic-Kralj L. Solid-phase microextraction. TrAC Trends in Analytical Chemistry 1999; 18: 272-282. doi: 10.1016/S0165-9936(98)00109-5

10. Li J, Wang YB, Li KY, Cao YQ, Wu S et al. Advances in different configurations of solid-phase microextraction and their applications in food and environmental analysis. TrAC Trends in Analytical Chemistry 2015; 72: 141-152. doi: 10.1016/j.trac.2015.04.023

11. Bagheri H, Roostaie A. Aniline-silica nanocomposite as a novel solid phase microextraction fiber coating. Journal of Chromatography A 2012; 1238: 22-29. doi: 10.1016/j.chroma.2012.03.027

12. Mehdini A, Aziz-Zanjani MO. Recent advances in nanomaterials utilized in fiber coatings for solid-phase microextraction. TrAC Trends in Analytical Chemistry 2013; 42: 205-215. doi: 10.1016/j.trac.2012.09.013

13. Er EO, Maltepe E, Bakirdere S. A novel analytical method for the determination of cadmium in sorrel and rocket plants at ultratrace levels: magnetic chitosan hydrogels based solid phase microextraction-slotted quartz tube-flame atomic absorption spectrophotometry. Microchemical Journal 2018; 143: 393-399. doi: 10.1016/j.microc.2018.08.019

14. Cheng LD, Pan SH, Ding CY, He J, Wang CY. Dispersive solid-phase microextraction with graphene oxide based molecularly imprinted polymers for determining bis(2-ethylhexyl) phthalate in environmental water. Journal of Chromatography A 2017; 1511: 85-91. doi: 10.1016/j.chroma.2017.07.012

15. Ye N, Shi P. Applications of graphene-based materials in solid-phase extraction and solid-phase microextraction. Separation and Purification Reviews 2015; 44 (3): 183-198. doi: 10.1080/15422119.2014.912664

16. Hou XD, Guo Y, Liang XJ, Wang XS, Wang L et al. Bis(trifluoromethanesulfonyl)imide-based ionic liquids grafted on graphene oxide-coated solid-phase microextraction fiber for extraction and enrichment of polycyclic aromatic hydrocarbons in potatoes and phthalate esters in food-wrap. Talanta 2016; 153: 392-400. doi: 10.1016/j.talanta.2016.03.034

17. Shahriman MS, Ramachandran MR, Zain NNM, Mohamad S, Manan NSA et al. Polyaniline-dicationic ionic liquid coated with magnetic nanoparticles composite for magnetic solid phase extraction of polycyclic aromatic hydrocarbons in environmental samples. Talanta 2018; 178: 211-221. doi: 10.1016/j.talanta.2017.09.023

18. Pang L, Yang PJ, Pang R, Lu XL, Xiao JW et al. Ionogel-based ionic liquid coating for solid-phase microextraction of organophosphorus pesticides from wine and juice samples. Food Analytical Methods 2018; 11 (1): 270-281. doi: 10.1007/s12161-017-0997-9

19. Rattana T, Chaiyakun S, Witit-anun N, Nuntawong N, Chindaudom P et al. Preparation and characterization of graphene oxide nanosheets. Procedia Engineering 2012; 32: 759-764. doi:10.1016/j.proeng.2012.02.009

20. Lyu Q, Yan H, Li L, Chen Z, Yao H et al. Imidazolium ionic liquid modified graphene oxide: as a reinforcing filler and catalyst in epoxy resin. Polymers 2017; 9 (9): article number 447. doi: 10.3390/polym9090447

21. Zhou X, Zhang Y, Huang Z, Lu D, Zhu A et al. Ionic liquids modified graphene oxide composites: a high efficient adsorbent for phthalates from aqueous solution. Scientific Reports 2016; 6: article number 38417. doi: 10.1038/srep38417

22. Heimer NE, Del Sesto RE, Meng Z, Wilkes JS, Carper WR. Vibrational spectra of imidazolium tetrafluoroborate ionic liquids. Journal of Molecular Liquids 2006; 124: 84-95. doi: 10.1016/j.molliq.2005.08.004

23. Botas C, Álvarez P, Blanco P, Granda M, Blanco C et al. Graphene materials with different structures prepared from the same graphite by the Hummers and Brodie methods. Carbon 2013; 65: 156-164. doi:10.1016/j.carbon.2013.08.009

24. Dizaji AK, Mortaheb HM, Mokhtaran B. Noncovalently functionalized graphene oxide/graphene with imidazolium-based ionic liquids for adsorptive removal of dibenzothiophene from model fuel. Journal of Materials Science 2016; 51 (22): 10092-10103. doi: 10.1007/s10853-016-0237-5

25. Gionfriddo E, Souza-Silva EA, Pawliszyn J. Headspace versus direct immersion solid phase microextraction in complex matrixes: investigation of analyte behaviour in multicomponent mixtures. Analytical Chemistry 2015; 87: 8448-8456. doi: 10.1021/acs.analchem.5b01850

26. Meng Y, Anderson JL. Tuning the selectivity of polymeric ionic liquid sorbent coatings for the extraction of polycyclic aromatic hydrocarbons using solid-phase microextraction. Journal of Chromatography A 2010; 1217 (40): 6143-6152. doi: 10.1016/j.chroma.2010.08.007

27. Merdivan M, Pino V, Anderson JL. Determination of volatile polycyclic aromatic hydrocarbons in waters using headspace solid-phase microextraction with a benzyl-functionalized crosslinked polymeric ionic liquid coating. Environmental Technology 2017; 38 (15): 1897-1904. doi: 10.1080/09593330.2016.1240242

28. Yang H, Shan C, Li F, Han D, Zhang Q et al. Covalent functionalization of polydisperse chemically-converted graphene sheets with amine-terminated ionic liquid. Chemical Communications 2009; 26: 3880-3882. doi: 10.1039/b905085j

29. Shan C, Yang H, Han D, Zhang Q, Ivaska A et al. Electrochemical determination of NADH and ethanol based on ionic liquid-functionalized graphene. Biosensors and Bioelectronics 2010; 25 (6): 1504-1508. doi: 10.1016/j.bios.2009.11.009

30. Amiri A, Ghaem F. Carbon nanospheres covalently modified with polydimethylsiloxane on a porous sol–gel support for use in headspace solid-phase fiber microextraction of BTE. Microchimica Acta 2017; 184: 297-305. doi: 10.1007/s00604-016-2019-9

31. Zhang H. Lee HK. Plunger-in-needle solid-phase microextraction with graphene-based sol–gel coating as sorbent for determination of polybrominated diphenyl ethers. Journal of Chromatography A 2011; 1218: 4509-4516. doi: 10.1016/j.chroma.2011.05.016

32. Zhang S, Du Z, Li G. Layer-by-layer fabrication of chemical-bonded graphene coating for solid-phase microextraction. Analytical Chemistry 2011; 83 (19): 7531-7541. doi: 10.1021/ac201864f

33. Ke Y, Zhu F, Jiang R, Wang Y, Yue L et al. Determination of polycyclic aromatic hydrocarbons in leather products using solid-phase microextraction coupled with gas chromatography-mass spectrometry. Microchemical Journal 2014; 112: 159-163. doi: 10.1016/j.microc.2013.10.010

34. Es-haghi A, Hosseininasab 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. Analytica Chimica Acta 2014; 813: 48-55. doi: 10.1016/j.aca.2014.01.005

35. Xu L, Feng J, Li J, Liu X, Jiang S. Graphene oxide bonded fused-silica fiber for solid phase microextraction gas chromatography of polycyclic aromatic hydrocarbons in water. Journal of Separation Science 2012; 35 (1): 93-100. doi:10.1002/jssc.201100612

36. Jin P, Zhou S, Wang H, Wang Z, Wang X et al. Electrophoretic deposition hyphenated with electrochemical anodization for the fabrication of phenyl-functionalized mesoporous silica onto Nitinol fibers for selective solid-phase microextraction of polycyclic aromatic hydrocarbons. Analytical Methods 2017; 9: 6459-6467. doi: 10.1039/c7ay02183f

37. Kazemipour M, Behzadi M, Ahmad R. Poly(o-phenylenediamine-co-o-toluidine)/ modified carbon nanotubes composite coating fabricated on a stainless steel wire for the headspace solid-phase microextraction of polycyclic aromatic hydrocarbons. Microchemical Journal 2016; 128: 258-266. doi: 10.1016/j.microc.2016.05.004