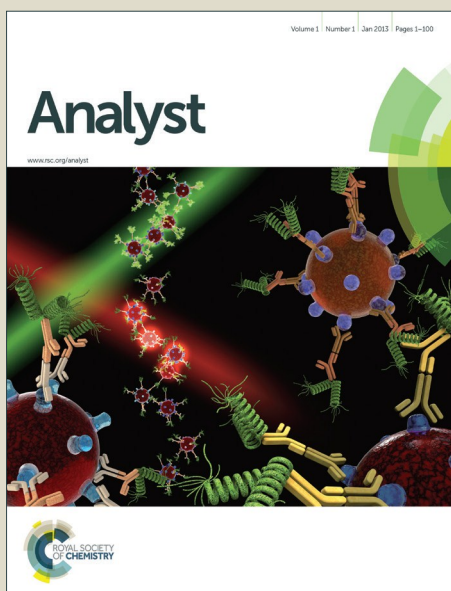


# Analyst

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## Analyst

## ARTICLE

## Ionogel fibres of bis(trifluoromethylsulfonyl)imide anion-based ionic liquids for the headspace solid-phase microextraction of chlorinated organic pollutants

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Ionogels, a family of hybrid materials in which ionic liquids (IL) are confined in a sol-gel network, are receiving much attention in a variety of scientific and technological fields. In this work, ionogels derived from three different ILs based on the anion bis(trifluoromethylsulfonyl)imide (TFSI), namely 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([C4C1Py][TFSI]), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C4C1Pyr][TFSI]), and 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide ([C4C1Pip][TFSI]) were obtained on the outer surface of optical fibres by sol-gel technology. The obtained hybrid materials were characterized by scanning electron microscope (SEM) and energy dispersive X-ray spectrometry (EDX), and subsequently evaluated as sorbent coatings for the headspace solid-phase microextraction (HS-SPME) of volatile chlorinated organic compounds in combination with gas chromatography with barrier ionization discharge detection (GC-BID). The ionogel based on [C4C1Pyr][TFSI] exhibited the highest extractability for target analytes. The experimental parameters that affect the extraction process were optimized by means of a central composite design. Under optimal conditions, the proposed method yielded excellent enrichment factors (EFs) in the range 3889-20919 and limits of detection (LODs) between 11 and 151 ng L<sup>-1</sup> for the target compounds. The inter-day repeatability, intra-day reproducibility and fibre-to-fibre reproducibility, were less than 8.5, 9.6 and 16.9%, respectively. Finally, the developed method was applied to the analysis of water samples, showing recovery values in the range 95-106%.

### Introduction

Solid-phase microextraction (SPME) is a miniaturized sample preparation technique that integrates sampling, extraction, preconcentration, clean-up and sample introduction.<sup>1</sup> Firstly introduced in the early 90's,<sup>2</sup> SPME has become widely used in a variety of scientific and technological fields due to its exceptional performance. A number of fibre coatings are nowadays commercially available. Unfortunately, they are not free from drawbacks; limited lifetime, fragility, significant batch-to-batch variation and limited sorption capacity are major concerns. In recent years, advances have been made toward the development of efficient alternatives to commercial SPME fibre coatings, including conducting polymers, molecularly imprinted polymers, sol-gel coatings, immunosorbents, metal organic frameworks, nanomaterials and ionic liquids (ILs).<sup>3-5</sup> The latter materials are characterized for their good extractability, high chemical and thermal

stability and negligible volatility, which make them especially suitable for extraction processes.<sup>6</sup> However, the implementation of ILs in SPME fibres has presented some difficulty so far. A number of strategies have been reported in the literature since the first approach published a decade ago which, basically, consisted on a disposable fibre where the IL was physically adsorbed by a dip-coating method.<sup>7</sup> Among the advances in this challenging field, polymeric ILs (PILs)-based sorbent coatings have remarkably shown improved robustness, reusability and stability.<sup>8</sup> A number of SPME fibres prepared with ILs and PILs-based have been proposed for the determination of diverse analytes.<sup>8-15</sup> The current state of the art of IL- and PIL-based SPME fibre coatings has been presented in excellent reviews.<sup>16-18</sup>

Recently, we have reported on the applicability of ionogels as SPME fibre coatings.<sup>19</sup> Specifically, the IL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was confined in a sol-gel network, showing excellent extractability toward a variety of volatile organic compounds. Ionogels are emerging hybrid materials where an IL is physically entrapped into a sol-gel matrix.<sup>20,21</sup> ILs behave as structuring media in the preparation of ionogels, and the physicochemical properties of ILs markedly influence the properties of the solid host network.<sup>22</sup> As a consequence of the tunable properties of ILs depending on their constituents, the composition of ionogels

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can be carefully adjusted for improved performance. Ionogels are awaking much interest in a broad range of disciplines, as described in recent review articles.<sup>22–24</sup>

In this work, three bis(trifluoromethylsulfonyl)imide anion-based ILs were used to prepare ionogel fibres by sol-gel technology. The resulting fibres were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) and evaluated for the extraction of seven chlorinated organic pollutants, some of them being included as priority substances in the field of water policy according to the European Water Framework Directive 2008/105/EC.<sup>25</sup> The optimum fibre coating was applied to the determination of these target analytes in water samples. The main text of the article should appear here with headings as appropriate.

## Experimental section

### Reagents and materials

Chlorinated organic compounds, namely hexachloroethane (HCE), hexachlorobutadiene (HCBD), 1,2-dichlorobenzene (1,2-DCB), 1,3-dichlorobenzene (1,3-DCB), 1,4-dichlorobenzene (1,4-DCB), 1,2,4-trichlorobenzene (1,2,4-TCB) and 2-chloronaphthalene (2-CN) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Methanol HPLC grade and n-hexane were obtained from Sigma Aldrich. Deionized water obtained from a Millipore Q system (Millipore, Molsheim, France) was used throughout. Standard solutions of target analytes were prepared in methanol by appropriate dilution of a stock solution of 2000  $\mu\text{g mL}^{-1}$  of each component in n-hexane, and working solutions were obtained by subsequent dilution of the standard solutions with deionized water. The ILs 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ( $[\text{C}_4\text{C}_1\text{Py}][\text{TFSI}]$ ), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ( $[\text{C}_4\text{C}_1\text{Pyr}][\text{TFSI}]$ ), and 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide ( $[\text{C}_4\text{C}_1\text{Pip}][\text{TFSI}]$ ) were purchased from Iolitec (Heilbronn, Germany). Methyltrimethoxysilane (MTMS) was purchased from Fluka (Buchs, Switzerland). Trifluoroacetic acid (TFA) and sodium sulfate were obtained from Sigma-Aldrich. Optical fibres with a 150  $\mu\text{m}$  diameter glass core and protective polyimide coating (Cezar Int., Poland) were used for obtaining the ionogel SPME fibres. Sulfuric acid, hydrochloric acid and sodium hydroxide were obtained from POCH (Gliwice, Poland) and used for the pretreatment of the glass substrates. Two commercial SPME fibres, namely 100  $\mu\text{m}$  polydimethylsiloxane (PDMS) and 85  $\mu\text{m}$  polyacrylate (PA), were purchased from Supelco (Bellefonte, PA).

### Instrumentation

All analyses were performed using a Shimadzu Tracera system. It consisted of a Shimadzu GC-2010 Plus capillary gas chromatograph coupled with a Shimadzu barrier ionization discharge (GC-BID) detector (BID-2010 Plus) (Shimadzu Scientific Instruments, Inc., Columbia, MD). An HP-5MS column (30 m x 0.25 mm, film thickness 0.25  $\mu\text{m}$ ) was used during the

experiments. The injector was operated in the splitless mode and maintained at 220  $^{\circ}\text{C}$ . Helium was used as the carrier gas. The column oven was programmed from 35  $^{\circ}\text{C}$  (10 min) at 20  $^{\circ}\text{C min}^{-1}$  to 125  $^{\circ}\text{C}$ , and then to 280  $^{\circ}\text{C}$  (2 min) at 10  $^{\circ}\text{C min}^{-1}$ . The temperature of the BID detector was set at 280  $^{\circ}\text{C}$ .

A scanning electron microscope (SEM) (Hitachi, model S-3400N) and an energy dispersive X-ray spectrometer system (EDX) (Thermo Fisher, model NSS 312) were used to evaluate the surface morphology and elemental composition of ionogel fibre coatings, respectively.

### Preparation of the SPME coatings

The preparation of ionogel-based SPME fibres involved four consecutive steps, namely pretreatment of the glass fibre, preparation of the sol solution, sol-gel coating of the SPME fibre *via* dip-coating, and thermal conditioning of the SPME fibre, as described in a previous work.<sup>19</sup>

The protective polyimide coating of the optical fibre was initially removed by means of conc.  $\text{H}_2\text{SO}_4$ , and the obtained glass fibres were pretreated to obtain a high density of surface silanol groups. Specifically, they were initially dipped in 1 mol  $\text{L}^{-1}$  NaOH for 1 h and rinsed with water, then dipped in a 0.1 mol  $\text{L}^{-1}$  solution of HCl for 30 min to neutralize the excess NaOH, washed with distilled water, allowed to dry at room temperature and stored in a desiccator for no more than 12 h before use.

Sol solutions were prepared by setting the molar ratio at 2/2/1 for IL/TFA/MTMS, respectively. Thus, sol solutions were obtained by adding the appropriate volume of a given IL (221.7  $\mu\text{L}$  of  $[\text{C}_4\text{C}_1\text{Pip}][\text{TFSI}]$ , 213.2  $\mu\text{L}$  of  $[\text{C}_4\text{C}_1\text{Py}][\text{TFSI}]$  or 212.3  $\mu\text{L}$  of  $[\text{C}_4\text{C}_1\text{Pyr}][\text{TFSI}]$ ), 56.4  $\mu\text{L}$  of TFA (95% v/v) and 50.0  $\mu\text{L}$  of MTMS into a plastic Eppendorf tube, mixing thoroughly after each addition.

Ionogel fibres were then obtained by following a dipping-coating method, which allowed a precise control of the film thickness. Thus, a pretreated glass fibre was dipped vertically into the sol solution for 1 min and subsequently withdrawn for 1 min with the pulling rate set at 160  $\text{mm min}^{-1}$ . Several dipping and drying steps were carried out to obtain an ionogel with the required film thickness on the outer surface of the glass fibre. Ionogel fibres were obtained in 30 min following this procedure. Finally, the obtained ionogel fibres were placed in a desiccator for 12 h, installed into a commercial SPME device (Supelco, Bellefonte, PA) and thermally conditioned at 230  $^{\circ}\text{C}$  for 1 h in the injection port of the GC.

### SPME procedure

12 mL of a salted (20%, w/v  $\text{Na}_2\text{SO}_4$ ) aqueous standard solution or water sample was placed into a 15 mL glass vial containing a glass-coated stir bar and sealed with a screw cap with a Teflon faced septum. Each sample solution was stirred at the highest stirring rate (1800 rpm) and thermostated at 30  $^{\circ}\text{C}$  for 10 min before extraction to reach thermal equilibrium. Then, the ionogel fibre was exposed to the headspace above the aqueous sample solution during 20 min for enrichment of target compounds. After extraction, the fibre was removed from the vial and immediately transferred to the GC injector



port, where the analytes were thermally desorbed at 220 °C for 10 min. These conditions proved to be sufficient to ensure complete desorption with no carryover.

## Results and discussion

### Preparation and characterization of [TFSI]-based ionogel fibres

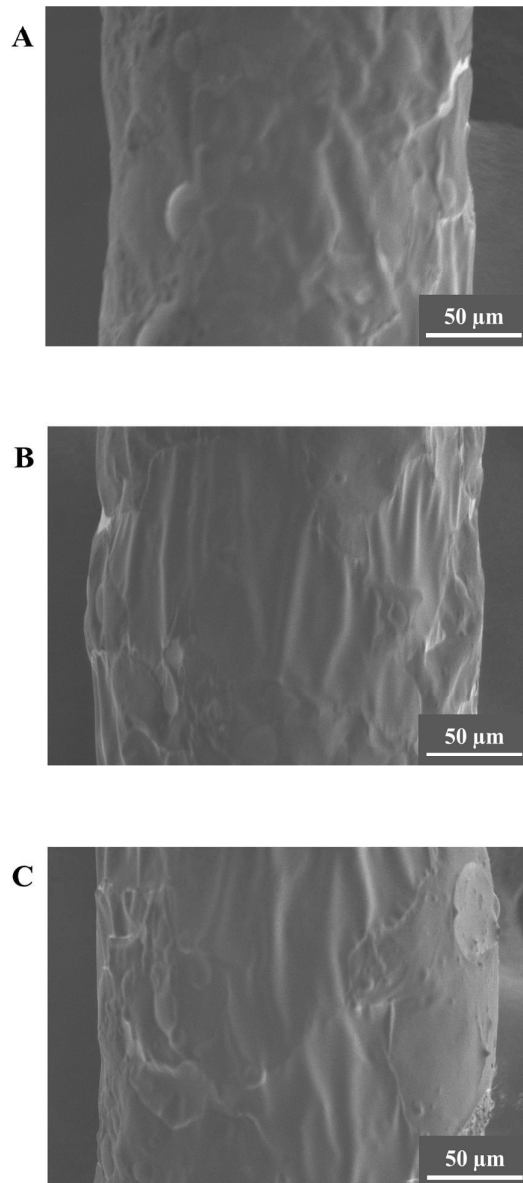
The ionogel fibres were prepared by sol-gel technology, according to a procedure described elsewhere.<sup>19</sup> The process involved the formation of a macromolecular network of sol-gel materials onto the external surface of a glass fibre by means of two types of reactions, namely hydrolysis and polycondensation. A number of ILs based on the [TFSI] anion were selected in this work as both solvent and porogenous agent in the sol-gel process. Their high thermal stability, low viscosity and relative hydrophobicity were considered advantageous aspects for their use in SPME. MTMS was used as the sol-gel precursor, and TFA as the acidic catalyst. The materials thus obtained consist on a solid-like tridimensional sol-gel network where the IL is physically confined.

The surface morphology of the ionogel fibres was evaluated by SEM. Figure 1A-C shows the SEM micrographs of the three evaluated ionogels. It can be observed that all three ionogel fibres present a homogeneous and rough surface. The average film thickness of prepared fibres was also estimated by means of SEM and found to be in the range 23-30 µm for the ionogel fibres prepared from [C<sub>4</sub>C<sub>1</sub>Pip][TFSI], [C<sub>4</sub>C<sub>1</sub>Py][TFSI] and [C<sub>4</sub>C<sub>1</sub>Pyrr][TFSI], respectively.

The elemental composition of the three ionogel fibres was evaluated by EDX analysis. The elemental mapping images obtained for the three fibres are shown in Figure S1. It can be clearly observed from the figure the presence of C, O, N, F, Si and S in all the three fibres evaluated. Remarkably, the density of these elements is practically constant in all of the evaluated fibres. The presence of N, S and F elements homogeneously distributed in the evaluated fibres can be assigned to the TFSI anion, which demonstrates the successful confinement of the three ILs in each sol-gel network.

### Comparative evaluation of SPME fibre coatings

The extractability of volatile chlorinated organic compounds by a number of SPME fibre coatings was evaluated for comparison purposes. Thus, the sorption capability of three [TFSI]-based ionogel fibres and two commercial fibres, namely PDMS and PA, were assessed by using the HS-SPME mode. Enrichment factors (EFs) were calculated as the ratio of the analyte concentration in the SPME fibre and the analyte concentration in the aqueous sample. As shown in Figure 2, the ionogel fibres yielded excellent EFs for the analytes of interest, the extractability of these compounds being dependent on the nature of the IL used. EFs in the range 1428-20910 were obtained with the three evaluated [TFSI]-based ionogel coatings. These values are, in average, 2.3 and 3.7 times higher than obtained with both PDMS and PA commercial fibres, respectively. It can also be deduced from Figure 2 that the ionogel based on the IL [C<sub>4</sub>C<sub>1</sub>Pyrr][TFSI]

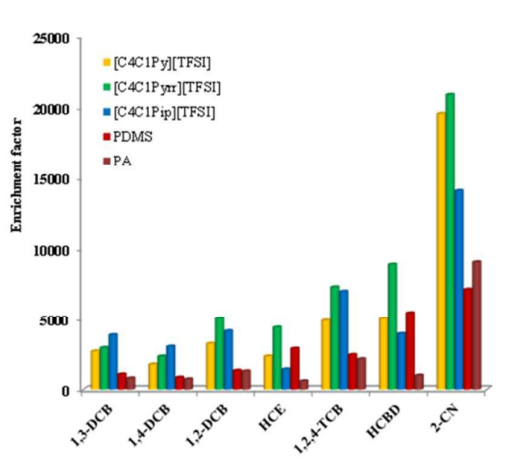


**Figure 1** SEM images of ionogel fibres prepared from (A) [C<sub>4</sub>C<sub>1</sub>Py][TFSI], (B) [C<sub>4</sub>C<sub>1</sub>Pyrr][TFSI] and (C) [C<sub>4</sub>C<sub>1</sub>Pip][TFSI] ILs, respectively.

showed the best extractability toward the evaluated analytes. Specifically, EFs in the range 2337-20910 were found when this ionogel fibre was used, which meant an average EF improvement of 2.6 and 4.7 times with regards to PDMS and PA, respectively. In accordance with these results, the [C<sub>4</sub>C<sub>1</sub>Pyrr][TFSI]-based ionogel coating was selected for further experiments.

### Optimization of the HS-SPME method

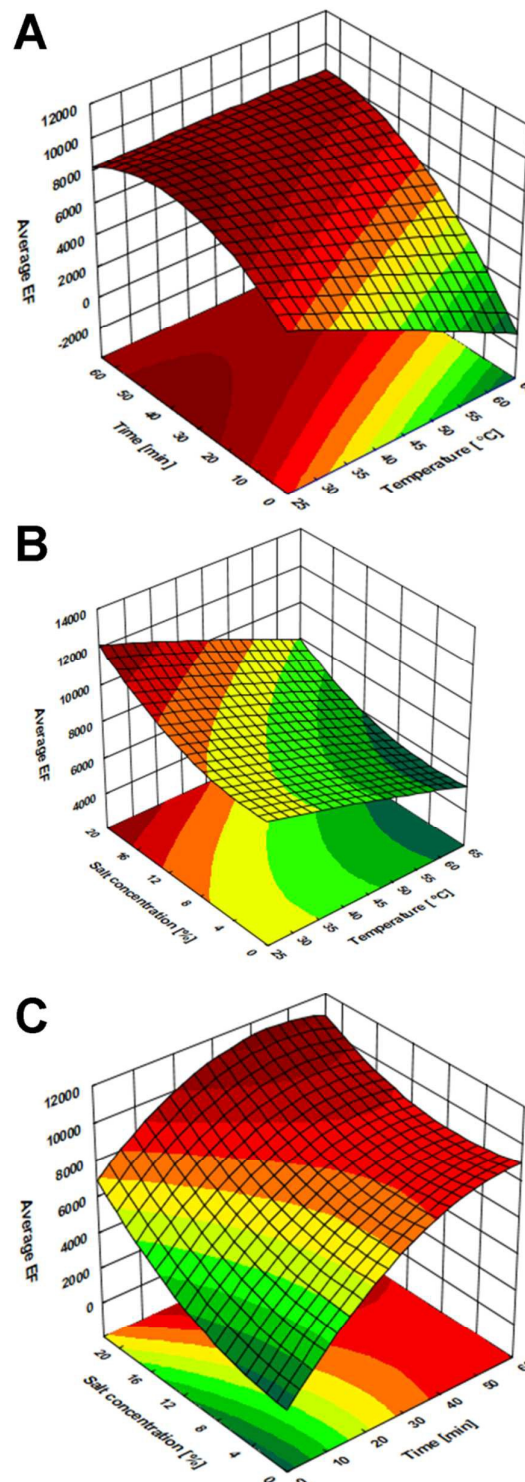
Several experimental factors have an influence on the extraction efficiency and should therefore be considered in the development of an HS-SPME method. Studies on the impact of extraction time, sample temperature, headspace volume,



**Figure 2** Comparison of the EFs achieved with the [TFSI]-based ionogels and commercial fibres. Experimental conditions: chlorinated organic pollutants concentrations,  $5 \mu\text{g L}^{-1}$ ; sample volume, 12 mL; sample temperature,  $40^\circ\text{C}$ ;  $\text{Na}_2\text{SO}_4$  concentration, 20% (w/v); equilibration time, 10 min; extraction time, 60 min; desorption temperature,  $220^\circ\text{C}$ ; desorption time, 10 min.

agitation method, stirring rate (if magnetic stirring was chosen), pH, salt addition, desorption time and temperature are often described in the literature. However, based on literature studies and previous experience, we decided to limit the number of factors to the following three: extraction temperature (it affects the partition of analytes between the different phases involved), extraction time (mass transfer processes are time dependent) and salt content (chlorinated compounds are known to be sensitive to the salt effect)<sup>15,19</sup>. The rest of the above mentioned parameters were not optimized and their values were set based on our previous experience.<sup>19</sup> Thus, the magnetic stirring was operated at the maximum available rotation speed (1800 rpm), whereas the headspace volume was kept at the minimum necessary for the fibre exposition in accordance with the well-known relationship describing the partitioning in three phase systems.<sup>26</sup> The desorption temperature was set at  $220^\circ\text{C}$ , that is,  $40^\circ\text{C}$  below the temperature in which  $[\text{C}_4\text{C}_1\text{Pyr}][\text{TFSI}]$  exhibits long-term thermal stability.<sup>27</sup> Under these conditions, a desorption time of 10 min was found to be sufficient to avoid carryover effects. A central composite design (CCD) was used for the optimization of extraction parameters. 7 central points were added to make the design orthogonal and rotatable. The final plan consisted of 23 runs, i.e. 8 factorial points, 6 star points, and 9 central points. The plan was generated by random sampling using Statistica 10 software package (StatSoft, USA). The values of the independent variables corresponding to specific experiments are shown in Table S1. The Table S1 also contains the values of the response variable for the extraction procedure, i.e. average EF for all studied analytes. The statistical significance of variables was evaluated by using the analysis of variance (ANOVA). The results are presented as Pareto chart in Figure S2. Taking into account statistical significance of two quadratic and one interaction terms, response surface functions were fitted to the obtained data using the model including linear main effects, quadratic

terms and two-factor interactions. The response surfaces plotted for the three combinations of independent variables are presented in Figure 3.



**Figure 3** Response surfaces obtained using the CCD as function of (A) extraction time vs temperature (salt concentration: 10% (w/v)), (B) temperature vs salt concentration (extraction time: 30 min), and (C) salt concentration vs extraction time (temperature:  $45^\circ\text{C}$ ).



**Table 1** Analytical characteristics of the HS-SPME-GC-BID method for determination of chlorinated organic pollutants

Analytes	EF	LOD ( $\mu\text{g L}^{-1}$ )	LOQ ( $\mu\text{g L}^{-1}$ )	Intra-day repeatability (RSD %, n=9)	Inter-day reproducibility (RSD %, n=3)	Fibre-to-fibre reproducibility (RSD %, n=3)	R <sup>2</sup>
HCE	5301	0.089	0.295	8.5	9.6	16.9	0.9994
HCBD	10419	0.024	0.079	6.7	7.3	16.7	0.9998
1,2-DCB	5351	0.104	0.347	6.0	7.2	13.0	0.9997
1,3-DCB	3889	0.151	0.503	5.8	7.0	8.2	0.9993
1,4-DCB	3895	0.015	0.051	4.6	7.8	10.9	0.9995
1,2,4-TCB	9449	0.011	0.037	5.7	6.7	13.2	0.9997
2-CN	20919	0.093	0.311	5.9	7.2	8.0	0.9998

The models obtained for [C<sub>4</sub>C<sub>1</sub>Pyrr][TFSI] ionogel fibres showed quite a good fit described by the respective R<sup>2</sup> values of 0.95. Based on the obtained results, a temperature equal to 30 °C and an extraction time of 30 min were chosen for further experiments. Application of a temperature slightly higher than room temperature does not cause significant loss in the EFs and, at the same time, simplifies the sample temperature control set up. A salt concentration of 20% (w/v) was chosen for practical reasons. Samples were stored at room temperature (20 °C) in which the water solubility of Na<sub>2</sub>SO<sub>4</sub> is close to 20% (w/v). It can be noticed from Figure 3C that the amount of retained analytes grows exponentially with time, however, after 30 min it reaches ca. 90% of that at 60 min (at 30 °C and salt concentration of 20% (w/v)). Therefore, the extraction time used in all subsequent experiments was set at 30 min.

#### Analytical performance

The analytical performance of the proposed method was evaluated under optimized experimental conditions. Results are summarized in Table 1.

The limits of detection (LOD) and quantification (LOQ) were calculated at a signal-to-noise ratio of 3 and 10, respectively. LODs and LOQs ranged from 0.011 to 0.151 and from 0.037 to 0.503  $\mu\text{g L}^{-1}$ , respectively, for all the target compounds. The calibration curves were linear from the LOQs to 100  $\mu\text{g L}^{-1}$  for all target analytes, with coefficients of determination in the range 0.9993-0.9998.

Under optimal conditions, the EFs obtained with the [C<sub>4</sub>C<sub>1</sub>Pyrr][TFSI]-based ionogel varied between 3889 and 20919 for the target analytes. These EFs correspond to extraction efficiencies from 4.7 to 25.3%.

The intra-day repeatability of the method, expressed as relative standard deviation (RSD), was assessed by consecutively extracting nine aqueous samples spiked at a 1  $\mu\text{g L}^{-1}$  level and found to be in the range 4.6-8.5%. In addition, the inter-day reproducibility, evaluated by carrying out the analyses in three consecutive days, varied between 6.7 and 9.6%. The fibre-to-fibre reproducibility was also assessed by

using three different [C<sub>4</sub>C<sub>1</sub>Pyrr][TFSI]-based ionogel fibres prepared under identical conditions for the extraction of the target analytes. The fibre-to-fibre reproducibility was found in the range 8.0-16.9%.

The fibre lifetime was evaluated throughout this work by carrying out a series of consecutive extraction/desorption cycles with a single [C<sub>4</sub>C<sub>1</sub>Pyrr][TFSI]-based ionogel fibre. Remarkably, the performance of the fibre was not significantly decreased after about 100 extraction/desorption cycles, so this can be assumed as the lifetime of the evaluated ionogel fibre.

The proposed method was finally applied to the determination of organic pollutants in tap and river water samples. Three replicate determinations were made for each sample. Analyte concentrations were found below the LOQ in both samples. Recovery studies were subsequently carried out to evaluate potential matrix effects. Thus, water samples were spiked at 1  $\mu\text{g L}^{-1}$  level with all target compounds and subjected to the optimized procedure. As shown in Table 2, the mean recoveries for the seven chlorinated compounds were in the range 95-106%. The obtained results thus revealed the feasibility of the proposed method for the determination of volatile chlorinated organics micropollutants in water samples by means of HS-SPME and GC-BID using the [C<sub>4</sub>C<sub>1</sub>Pyrr][TFSI]-based ionogel fibre.

**Table 2** Analytical results for the determination of chlorinated organic pollutants in spiked water samples

Analytes	Tap water		River water	
	Relative recovery (%)	RSD (%)	Relative recovery (%)	RSD (%)
HCE	96.7	5.4	105.0	9.3
HCBD	102.7	7.8	95.5	9.6
1,2-DCB	105.1	7.7	102.0	6.4
1,3-DCB	103.7	6.0	98.0	6.7
1,4-DCB	99.8	8.0	105.4	7.7
1,2,4-TCB	104.3	6.2	105.4	7.2
2-CN	105.6	6.5	98.9	7.2

## Conclusions

In this work, a number of ionogel-based SPME fibres were prepared by sol-gel reactions in the presence of three different ILs containing the TFSI anion. Remarkably, a different extractability was observed depending on the type of physically confined IL. The optimal SPME fibre, based on the [C<sub>4</sub>C<sub>1</sub>Pyrr][TFSI] IL, exhibited high extractability for a number of chlorinated organic micropollutants of environmental concern and remarkable durability (approximately 100 consecutive extraction/desorption cycles). According to the tunable properties of ILs, novel opportunities can be envisaged in extraction processes by suitable selection of the solid host network and guest IL combinations.

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