An Ionic Liquid as a Solvent for Headspace Single Drop Microextraction of Chlorobenzenes from Water Samples

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An ionic liquid as a solvent for headspace single drop microextraction of chlorobenzenes from water samples

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Abstract

A headspace single-drop microextraction (HS-SDME) procedure using room temperature ionic liquid and coupled to high-performance liquid chromatography capable of quantifying trace amounts of chlorobenzenes in environmental water samples is proposed. A Plackett–Burman design for screening was carried out in order to determine the significant experimental conditions affecting the HS-SDME process (namely drop volume, aqueous sample volume, stirring speed, ionic strength, extraction time and temperature), and then a central composite design was used to optimize the significant conditions. The optimum experimental conditions found from this statistical evaluation were: a 5 μL microdrop of 1-butyl-3-methylimidazolium hexafluorophosphate, exposed for 37 min to the headspace of a 10 mL aqueous sample placed in a 15 mL vial, stirred at 1580 rpm at room temperature and containing 30% (w/v) NaCl. The calculated calibration curves gave a high level of linearity for all target analytes with correlation coefficients ranging between 0.9981 and 0.9997. The repeatability of the proposed method, expressed as relative standard deviation, varied between 1.6 and 5.1% ($n = 5$). The limits of detection ranged between 0.102 and 0.203 μg L^{-1}. Matrix effects upon extraction were evaluated by analysing spiked tap and river water as well as effluent water samples originating from a municipal wastewater treatment plant.

Keywords: Chlorinated benzenes; Headspace single-drop microextraction (HS-SDME); Solvent microextraction; Ionic liquid; Water analysis; High-performance liquid chromatography (HPLC)

1. Introduction

Recently there is a strong move toward the miniaturization of chemical analysis systems since they have several distinct advantages (e.g., faster analysis, smaller sample volume and portability). In addition, an environmentally friendly feature of the miniaturized analysis systems is that the consumption of reagents is reduced. Miniaturization has reached most steps in quantitative analysis, and among them, sample preparation. Single-drop microextraction (SDME) is a miniaturization of the traditional liquid–liquid extraction (LLE) technique, whereby a microlitre drop of a water immiscible solvent is exposed to the sample solution achieving thus preconcentration of the target pollutants in a simple and fast step [1]. However, evaporation of the extracting solvent drop is an important drawback that deteriorates the method figures of merit.

Room temperature ionic liquids (ILs) are a group of new organic salts consisting of a combination of organic cations and various anions that are liquids at room temperature. Important features of ILs include their immeasurably low vapour pressure, high stability, large viscosity, moderate dissolvability of organic compounds as well as adjustable miscibility and polarity [2–5]. Recently the possibility of using ILs as the acceptor phase for SDME has been reported [6]. A 10 μL droplet of IL was immersed into the sample solution and recoveries ranging between 90 and 113% were obtained for two major alkylphenols (4-nonylphenol and 4-*tert*-octylphenol) in an aquatic environment. The main advantages of ILs when used for SDME are that they allow the application of longer sampling times as well as the use of larger drop volumes, thus leading to the development

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of high-performance liquid chromatography (HPLC) protocols with increased sensitivity.

Chlorobenzenes are listed priority hazardous substances [7–9] constituting a serious environmental concern given that biological accumulation can be expected to occur once they enter the aquatic ecosystem [10]. Despite their acute toxicity they are widely used as raw materials and intermediates in the manufacture of pesticides and chlorinated phenols, and as process solvents and as such they may enter the aquatic environment through solid and liquid effluents as well as atmospheric discharges [11].

In general, trace determination of chlorobenzenes in water is usually performed by gas chromatography coupled with a sample pre-treatment step such as the traditionally used liquid–liquid extraction (LLE) [12,13], or even the more recently introduced solid-phase extraction [14,15] and solid-phase microextraction techniques [16]. We have recently reported the applicability of headspace single-drop microextraction for the extraction of chlorobenzenes in aqueous samples [17]. The developed method proved to be an excellent preconcentration tool and according to the results, exposing a microlitre organic solvent drop to the headspace of an aqueous sample contaminated with 10 chlorobenzene compounds prior to gas chromatography–mass spectrometry, yielded detection as well as quantification of the target pollutants in the $\mu g\,L^{-1}$ concentration level. However, the liquid organic drop evaporates decreasing the droplet size that deteriorates precision and sensitivity. The latter figure of merit is reduced due to the shortening on sampling times.

Advantageous properties of ILs are especially attractive for efficient SDME. The use of an ionic liquid as the acceptor/extractant phase afforded more reproducible extraction conditions, the application of longer extraction times as well as the use of a larger drop volume. 1-butyl-3-methylimidazolium hexafluorophosphate [C_4MIM][PF_6] is one of the ILs most commonly used in microextraction [18,19]. Therefore, the possibility of using [C_4MIM][PF_6] for the determination of chlorobenzenes in environmental water samples using headspace SDME coupled to HPLC is evaluated.

In general, the traditional methods of optimization evaluate the effect of one variable at-a-time, keeping all the others variables constant during experiments with the exception of the one being evaluated. This type of experiment does not allow to determine interaction between variables nor the statistical significance of the variables. However, experimental design, a multivariate optimization strategy, enables estimating simultaneously the effects of several variables alleviating the limitations described above. As a result fewer measurements than the classical one-at-a-time experiment are required yielding however, the same precision.

The main objective of this study was to evaluate the possibility of using an IL during the headspace SDME of chlorobenzenes from water samples. For the purpose of these studies 1-butyl-3-methylimidazolium hexafluorophosphate [C_4MIM][PF_6] was used as the extractant IL phase. Variables, such as, drop volume, aqueous sample volume, stirring speed, ionic strength, extraction time and temperature were optimized by a multivariate strategy based on an experimental design using a Plackett–Burman design for screening and a central composite design for optimizing the significant parameters and the optimized procedure was applied to determine chlorobenzenes in aqueous samples.

2. Experimental

2.1. Chemicals and solutions

1,2-Dichlorobenzene (1,2-DCB), 1,4-dichlorobenzene (1,4-DCB), 1,3-dichlorobenzene (1,3-DCB), 1,2,3-trichlorobenzene (1,2,3-TCB), 1,2,4-trichlorobenzene (1,2,4-TCB), 1,3,5-trichlorobenzene (1,3,5-TCB), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB) and 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB) were obtained from Riedel-de Haën (Seelze, Germany). The internal standard solution consisted of a methanol solution of 1,4-dibromobenzene (1,4-DBB) (Riedel-de Haën, Seelze, Germany). Methanol and acetonitrile were HPLC-grade and were obtained from Scharlau Chemie (Barcelona, Spain). Deionised water was prepared on a water purification system (Milli-Q Biocel A10) supplied by Millipore (Billerica, MA, USA).

Synthesis-grade ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [C_4MIM][PF_6], was obtained from Merck (Darmstadt, Germany). Sodium chloride (Merck, Darmstadt, Germany) was used to adjust the ionic strength of the aqueous samples. Stock standard solutions of $1000\,mg\,L^{-1}$ of target compounds were prepared in methanol. Working solutions were prepared by dilution of standard stock solutions. All solutions were stored in the dark at 4 °C.

2.2. Environmental water samples

Tap water from the main area water-supply network of San Vicente del Raspeig (Alicante, Spain), river water from the Ebro river (Spain) and effluent water (Bilbao, Spain) from a municipal wastewater treatment plant were used for the recovery studies. Samples were collected in 250 mL Pyrex borosilicate ambar glass containers with caps, lined with aluminium foil, stored in the dark at 4 °C and were analysed without previous treatment or filtration within 48 h of collection. Initial analysis confirmed that they were free of all target analytes.

2.3. Headspace SDME

The general headspace SDME procedure followed in the present studies was according to our previous guidelines [17]. In short and unless otherwise stated within the text, 10 mL of a freshly prepared aqueous solution, spiked at a known concentration with all target analytes and containing 30% (w/v) NaCl, was placed in a 15 mL crimp top glass vial. A home-made glass coated stirring bar was added and a Mininert valve (Supelco, Bellefonte, PA, USA) was fitted to the vial. Magnetic stirring at the stirrer's maximum speed (1580 rpm) was then applied. For all quantification experiments, aqueous samples were also spiked with a known amount of the internal standard solution.

A 3 mm long polytetrafluoroethylene (PTFE) tube (i.d.: 0.8-mm; o.d.:1.6-mm) was fitted to the blunt needle tip of a 25 μL Hamilton Gastight syringe (Model 1702 Hamilton Bonaduz AG,

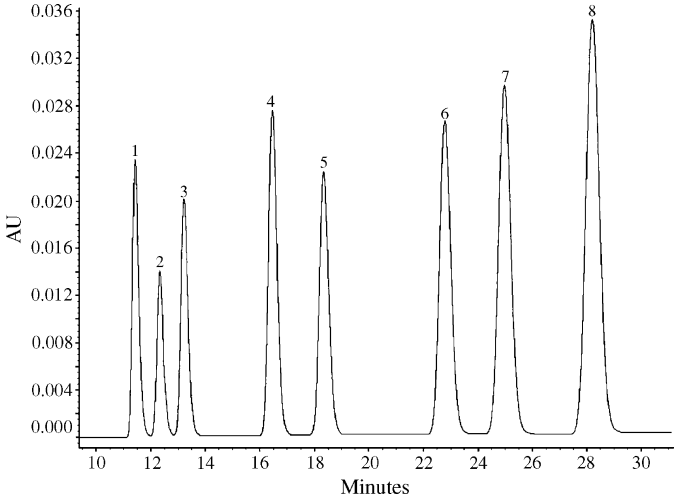

Fig. 1. Typical chromatogram of chlorobenzenes studied. (1) 1,2-DCB; (2) 1,4-DCB; (3) 1,3-DCB; (4) 1,2,3-TCB; (5) 1,2,4-TCB; (6) 1,3,5-TCB; (7) 1,2,3,4-TeCB; and (8) 1,2,4,5-TeCB. λ = 210 nm. IL elutes firstly showing a broad peak (mean retention time: 3.0 min).

Bonaduz, Switzerland; length: 5.1 cm, i.d.: 0.015 cm), maximising thus the contact area between the drop and the needle tip. The microsyringe, typically contained 5 μL of the ionic liquid acceptor phase, was clamped above the vial and its needle passed through the Mininert valve until its tip was 1 cm below the lower surface of valve. The plunger was depressed and a microdrop of the ionic liquid phase was exposed to the headspace above the sample at room temperature typically for 37 min. After extraction, the microdrop was retracted into the microsyringe, the PTFE tube was removed and the acceptor phase was injected into the HPLC system for analysis.

2.4. HPLC determination

The HPLC equipment included a Waters 600E System Controller and a Waters 996 Photodiode Array Detector (PDA) set at 210 nm (Milford, MA, USA). A personal computer equipped with a Milenium32 Waters program for LC systems was used to process all chromatographic data. A 7725i Rheodyne injector (Rohnert Park, CA, USA) and a Phenomenex Luna C_{18} column (150 mm × 4.6 mm, 5 μm particle size) were used, respectively, for injection and separation of the target analytes. The mobile phase was a 65:35 (v/v) mixture of acetonitrile–water and the flowrate was set at 1 mL min^{-1}. Fig. 1 shows a typical chromatogram.

2.5. Data processing

Statgraphics Statistical Computer Package "Statgraphics Plus 5.1" was used to construct experimental design matrices and evaluate the results.

3. Results and discussion

3.1. Screening design

Screening is the first step in the efficient assessment of the factors involved in the studied analytical system. If a large number of factors are involved, reduced factorial designs are employed. A particular type of those designs is the Plackett–Burman design [20,21], which assumes that the interactions can be completely ignored and so the main effects are calculated with a reduced number of experiments. In this work, six variables were selected to define the experimental field with two levels for each factor. The variables considered in the present studies were ionic strength, drop volume, aqueous sample volume, extraction time, stirring speed, and extraction temperature and the examined levels are given in Table 1.

Table 1
Experimental variables and levels of the Plackett–Burman design

Variable	Level	
	Low	High
Ionic strength (NaCl concentration; %, w/v)	0	30
Drop volume (μL)	5	10
Sample volume (mL)	5	10
Extraction time (min)	10	30
Stirring speed (rpm)	0	1580
Extraction temperature (°C)	25	55

A Plackett–Burman design was applied to evaluate the main effects. The overall design matrix shows 12 runs randomly carried out trying to nullify the effect of extraneous or nuisance variables. The data obtained were evaluated by ANOVA test and the results were visualized by using main effects Pareto charts shown in Fig. 2. The charts for 1,3-DCB and 1,4-DCB, 1,3,5-TCB and 1,2,3-TCB, and 1,2,3,4-TeCB are not shown since they are similar to 1,2-DCB, 1,2,4-TCB and 1,2,4,5-TeCB, respectively. In Fig. 2 the bar lengths are proportional to the absolute value of the estimated main effect and a vertical reference line corresponding to the 95% confidence interval is included for each Pareto chart. An effect which exceeds this vertical reference line may be considered significant with regard to the response. Furthermore, the positive or negative sign (corresponding to a black or white bar filling) reveals the cases when the instrument's response can be enhanced or reduced, respectively, when passing from the lowest to the highest level set for the specific factor.

According to Fig. 2, in this study, the extraction time is the most significant variable having a positive sign for all target analytes. Extraction temperature is the next most significant variable for five, the more chlorinated and relatively less volatile chlorobenzene compounds, of the eight analytes, showing a positive effect for all the analytes studied. Sodium chloride concentration does not appear as a significant variable in the Pareto chart but it was chosen as the next most significant variable because of the results given by the normal probabilistic plots (not included) for some of the analytes and according to previous experiments of the same type which proved the influence of this variable on the extraction efficiency [22]. Sodium chloride showed a positive effect upon extraction and the effect appears to be more pronounced in the case of the less chlorinated organic contaminants.

Fig. 2 also reveals that sample volume appeared to have a positive yet non-significant effect upon extraction. In general, increasing the aqueous sample volume results in an increase of

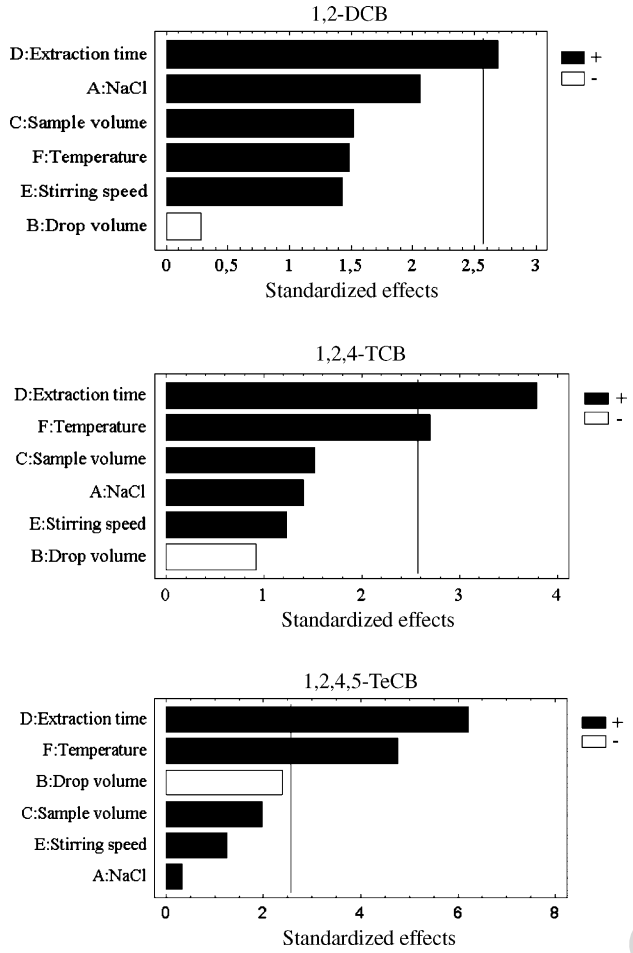

Fig. 2. Pareto charts of the main effects obtained from Plackett–Burman design for 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and 1,2,4,5-tetrachlorobenzene.

the total amount of target pollutants transferred in the headspace, enhancing thus preconcentration. A similar conclusion can be made in the case of the effect of stirring speed upon extraction. Increasing the speed of sample stirring is expected to enhance the rate of extraction of all target analytes, and this is a positive yet non-significant effect as shown in the Pareto charts of Fig. 2.

Drop volume shows the only negative, yet, non-significant effect (Fig. 2). This negative effect is in agreement with previously published results [23,24] and is attributed to the fact that larger organic solvent drops require extended equilibration times given that mass transfer into the drop is by diffusion alone, representing thus a slow step in the overall extraction procedure [25].

Overall, the results of this first screening study revealed that three variables could be fixed (namely ionic liquid drop volume: 5 μL; volume of sample: 10 mL; and stirring speed: 1580 rpm) for the following optimization step.

3.2. Optimization design

The second step concerned the improvement of the analytical system's output, as a function of several experimental factors. Many designs for modelling are based on the central composite design (CCD, sometimes called a response surface design), which is constructed by several superimposed designs and consists of a factorial design (2^k) augmented with (2k) star points, and with central points (n) [20,26]. The star points were located at $+\alpha$ and $-\alpha$ from the centre of the experimental domain. An axial distance α was selected with a value of 1.682 in order to establish the rotatability condition of the central composite design. It is assumed that the central point for each factor is 0, and the design is symmetric around this. The runs at the centre of the experimental field were performed nine times. Therefore, the overall matrix of CCD design involved 23 experiments. This design was used to optimize and evaluate main effects, interaction effects, and quadratic effects. A 3-factor, 3-level design used is suitable for exploring quadratic response surfaces and constructing second-order polynomial models. The nonlinear computer-generated quadratic model is given as:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2$$

where x_1, x_2 and x_3 are the independent variables, β_0 an intercept, β_1–β_{33} are the regression coefficients and y is the response function (in our case, sum of the peak areas of all the target analytes obtained by HPLC). In light of this, the next step consisted of finding the optimum conditions of the three variables. In this study, the three variables considered were: sodium chloride concentration (ionic strength), extraction time and extraction temperature. The lower, central, and upper levels of these variables as well as the location of their star points are given in Table 2.

Table 2
Experimental variables, levels and star points of the central composite design (CCD)

Variable	Level			Star points ($\alpha = 1.682$)	
	Lower	Central	Upper	$-\alpha$	$+\alpha$
Ionic strength (NaCl concentration; %, w/v)	8	16	25	2	30
Extraction time (min)	10	20	30	3	37
Extraction temperature (°C)	25	37	50	17	70

It should be mentioned here that the overall optimum conditions were the same based on each individual analyte peak area, with all the other analytes in the matrix, and based on a response function sum of all the peak areas of target analytes. This is in accordance with several previous reports dealing with the optimization design of the solid-phase microextraction (SPME) conditions [27–29]. Accordingly, the response used in the present work was based on the sum of the peak areas (total area) of the HPLC-PDA analysis after extracting the target compounds with headspace SDME under the conditions of the central composite design.

The data obtained were evaluated by ANOVA test and the effects were visualized by using Pareto chart shown in Fig. 3. As can be seen, extraction time and sodium chloride concentration were the most important variables, both showing a positive effect. Interestingly, temperature was found to have

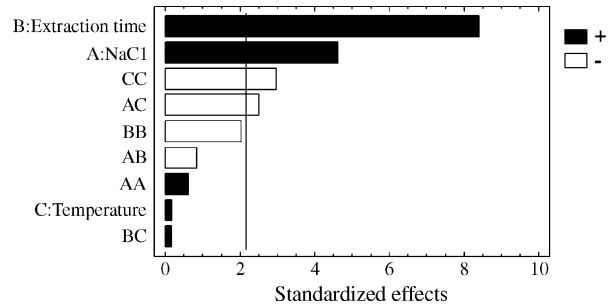

Fig. 3. Pareto chart of main effects in the central composite design for total chromatographic peak area. AA, BB and CC are the quadratic effects of sodium chloride concentration, extraction time and temperature, respectively. AB, AC, and BC are the interaction effects between sodium chloride concentration and extraction time, between sodium chloride concentration and temperature, and between extraction time and temperature, respectively.

a non-significant positive effect. Furthermore, examination of the effect (interaction) of one variable to another and quadratic effects also given in Fig. 3, revealed that the interaction between temperature and sodium chloride concentration (denoted as AC) and the quadratic effect of temperature (CC) [20] were statistically significant, exhibiting a negative effect upon extraction.

Given that it is not possible to plot simultaneously the response as a function of all the factors controlling the extraction process, the effects of pairs of factors were considered separately. Accordingly, the plots given in Fig. 4, are useful for interpreting graphically the variation of the instrument's response as a function of each pair of independent variables. Accordingly, Fig. 4a shows the instrument's response surface obtained by plotting sodium chloride concentration versus extraction time with the extraction temperature fixed at 37 °C, Fig. 4b shows the response surface developed for extraction time and extraction temperature, whilst keeping a sodium chloride concentration of the order of 16% (w/v) and finally, Fig. 4c shows the response surface obtained as a function of sodium chloride concentration and extraction temperature, for a set extraction time of the order of 20 min.

As can be seen, the presence of salt greatly enhances extraction for all target analytes (Fig. 4a and c), reaching a maximum at 30% (w/v) NaCl salt content. The positive effect of the addition of sodium chloride upon extraction has been discussed by many authors [30,31]. In general, addition of NaCl in the aqueous solution is expected to enhance extraction due to the salting-out effect where fewer water molecules are available for dissolving the analyte molecules, preferably forming hydration spheres around the salt ions [17,32]. This is expected to increase the total amount of analytes transferred in the headspace and as such enhance extraction [33,34].

The non-significant positive effect of temperature upon extraction shown in Fig. 3 is not confirmed by Fig. 4b and c. Fig. 4c confirms the existence of the significant negative interaction between sodium chloride and temperature, which reveals that room temperature is the optimum value upon extraction and Fig. 4b also reveals that the response of the analytical instrument is optimized when extracting the target analytes at room temperature. A previous report, dealing with the determination of

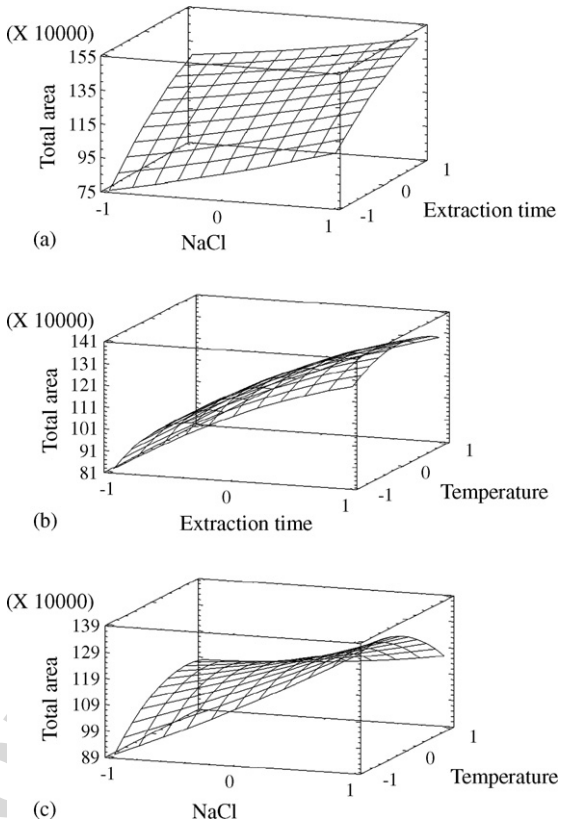

Fig. 4. Response surfaces for total chromatographic peak area using the central composite design obtained by plotting: (a) NaCl concentration vs. extraction time (extraction temperature: 37 °C); (b) extraction time vs. temperature (NaCl: 16%, w/v); and (c) NaCl concentration vs. temperature (extraction time: 20 min).

BTEX in water samples using IL-coated stainless steel wires investigated the effect of temperature (in the range of 0–50 °C) upon extraction [35]. The results revealed that peak areas of target analytes increased when increasing the temperature from 0 to 20 °C and then decreased for sampling temperatures from 20 to 50 °C. The authors concluded that although high temperatures increase diffusion coefficients of analytes in water and from liquid sample to the headspace, it may also decrease the partition coefficients of analytes in the IL fiber coating, thereby decreasing extraction efficiencies. Due to the similarities between both headspace ILs uses (coating fiber and single drop microextractions), accordingly, if a temperature increase results in a decrease of the rate of analyte adsorption on the outer surface of the microdrop then this is expected to reduce extraction.

From the second optimization study, the response of the analytical instrument is expected to be maximized in terms of total area for a sodium chloride concentration reaching the value of 30% (w/v) ($+\alpha$), extraction time reaching the value of 37 min ($+\alpha$) and extraction temperature reaching the value of 25 °C (-1). Overall, summarising the results of the two step optimization yields the following optimum experimental conditions: sodium chloride concentration, 30% (w/v); extraction time, 37 min; extraction temperature, 25 °C; drop volume, 5 μL; sample volume, 10 mL; and stirring speed, 1580 rpm.

3.3. Evaluation of headspace IL-SDME

Quality parameters of the proposed method were evaluated. In order to test the linearity, calibration studies were performed and the concentration range tested was from 5 to 160 $\mu g\,L^{-1}$ for all target analytes. The calculated calibration curves gave a high level of linearity for all target analytes with correlation coefficients (r) ranging between 0.9981 and 0.9997 as shown in Table 3. The repeatability of the proposed method, expressed as relative standard deviation (R.S.D.), was evaluated by extracting five consecutive aqueous samples (spiked at 20 $\mu g\,L^{-1}$ with each target analyte) and was found to vary between 1.6 and 5.1% with a mean value of 3.4% (Table 3). Indeed the use of ionic liquid as the acceptor phase in headspace SDME as well as the fact that HPLC instrumentation is used resulted in a net decrease of the R.S.D. values when compared to other headspace SDME methods used for the determination of chlorobenzenes in water [36].

Next, the limits of detection (LODs) for all target analytes were determined according to a signal-to-noise-ratio (S/N) of three and the limits of quantification (LOQs) as 10 times the above mentioned ratio. As can be seen in Table 3, the LODs and LOQs values were found to be in the low $\mu g\,L^{-1}$ level ranging between 0.102 and 0.203 $\mu g\,L^{-1}$ and between 0.338 and 0.677 $\mu g\,L^{-1}$, respectively. It should be mentioned here, that these values are considerably lower than the ones reported so far dealing with the HPLC analysis of aqueous samples containing chlorobenzenes [37,38].

Although there are no reports stating the influence of sample matrix upon the headspace SDME procedure, the feasibility of this liquid phase microextraction procedure must be demonstrated with real samples. Accordingly, method validation was also performed with three different environmental water samples, namely tap water, river water and effluent wastewater originating from a municipal wastewater treatment plant. Initial headspace SDME analyses of these samples did not show detectable concentrations of the target compounds and as such they were found suitable for recovery experiments. For the purpose of the present studies, eight replicate analyses under the optimized experimental conditions were performed for each type of environmental water. Relative recoveries were determined as the ratio of the concentrations found in real and deionised water samples spiked at the same contamination level (20 $\mu g\,L^{-1}$ for each target contaminant) [17,32]. The results for each set of experiments, summarised in Table 4, show that for the tap water samples relative recoveries ranged between 94 and 101%, with a mean value of 96%, for the river water samples between 99 and 107%, with a mean value of 102%, and for effluent water samples between 61 and 121%, with a mean value of 92%. As can be seen, the results revealed that relatively elevated R.S.D. values as well as decreased relative recoveries were observed for the more hydrophobic target pollutants (namely 1,2,3,4-tetrachlorobenzene and 1,2,4,5-tetrachlorobenzene) when examined in the effluent water matrix. This is most probably due to the fact that competitive adsorption to suspended solids can indeed reduce the effective

Table 3
Main method parameters for the extraction of chlorobenzenes from water samples using the optimized headspace ionic liquid SDME method

Analyte	Slope ± S.D.	Intercept ± S.D.	Correlation coefficient (r)[a]	R.S.D. (%)[b]	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)
1,2-DCB	0.109 ± 0.001	−0.038 ± 0.012	0.9997	5.1	0.102	0.338
1,4-DCB	0.065 ± 0.002	−0.116 ± 0.150	0.9981	2.3	0.203	0.677
1,3-DCB	0.090 ± 0.001	−0.022 ± 0.075	0.9997	5.0	0.152	0.508
1,2,3-TCB	0.171 ± 0.004	−0.039 ± 0.325	0.9987	1.6	0.102	0.338
1,2,4-TCB	0.141 ± 0.002	0.134 ± 0.139	0.9996	3.4	0.122	0.406
1,3,5-TCB	0.178 ± 0.003	0.146 ± 0.245	0.9993	4.1	0.122	0.406
1,2,3,4-TeCB	0.247 ± 0.003	0.358 ± 0.247	0.9996	3.1	0.102	0.338
1,2,4,5-TeCB	0.272 ± 0.005	0.750 ± 0.398	0.9992	3.0	0.102	0.338

[a] Linear range: 5–160 $\mu g\,L^{-1}$ (number of calibration points = 6).
[b] Relative standard deviation (R.S.D.); mean value for five replicate analyses; spiking level 20 $\mu g\,L^{-1}$.

Table 4
Relative recoveries and R.S.D. values of the eight chlorobenzenes studied in real water samples

Analyte	Relative recoveries (%) and R.S.D. values (%) in parentheses[a]		
	Tap water	River water	Effluent water
1,2-DCB	97.3 (4.2)	101.1 (5.8)	114.1 (3.2)
1,4-DCB	98.0 (3.1)	100.5 (1.9)	120.6 (2.4)
1,3-DCB	100.9 (6.5)	106.6 (3.1)	112.1 (3.8)
1,2,3-TCB	96.0 (1.3)	101.0 (2.1)	86.0 (2.8)
1,2,4-TCB	96.5 (1.7)	99.3 (2.5)	89.5 (5.1)
1,3,5-TCB	94.1 (2.0)	101.2 (4.5)	83.2 (4.4)
1,2,3,4-TeCB	95.9 (2.8)	101.6 (3.9)	60.8 (6.6)
1,2,4,5-TeCB	96.8 (2.8)	106.1 (3.1)	66.0 (6.8)

[a] Eight replicate analyses at a 20 $\mu g\,L^{-1}$ spiking level.

concentration of the analyte in the aqueous phase, therefore reducing the quantity of analyte transferred into the headspace and as a consequence the amount of analyte extracted into the acceptor phase. For the rest of the analytes, it appears that matrix had little effect upon extraction.

4. Conclusions

The multivariate optimization strategy used here, allowed the successful determination of the optimum conditions for the main operational parameters taken into consideration during headspace SDME. The resulting optimized procedure combined with the unique properties of IL (namely non-volatility and adequate viscosity) allowed quantification of trace levels of different polychlorinated benzenes in water samples whilst using a headspace SDME approach coupled to HPLC.

The "green character" of ILs has been recently questioned since some of them show dermal toxicity on fish [39]. However, the small droplet volume used on SDME reconciles ILs with the general environmental-friendliness of microextraction.

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References

[1] E. Psillakis, N. Kalogerakis, Trends Anal. Chem. 21 (2002) 53.
[2] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, Chem. Commun. 16 (1998) 1765.
[3] D.W. Armstrong, L. He, Y.-S. Liu, Anal. Chem. 71 (1999) 3873.
[4] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156.
[5] J.-F. Liu, G.-B. Jiang, Y.-G. Chi, Y.-Q. Cai, Q.-X. Zhou, J.-T. Hu, Anal. Chem. 75 (2003) 5870.
[6] J.-F. Liu, Y.-G. Chi, G.-B. Jiang, C. Tai, J.-F. Peng, J.-T. Hu, J. Chromatogr. A 1026 (2004) 143.
[7] World Health Organisation (WHO), 10th Report on Carcinogens, National Toxicology Program, Public Health Service, 2002.
[8] EC (European Community) Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Official Journal L 129, May 18, 1976.
[9] EC (European Community), 2000. Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for Community action in the field of water policy. Official Journal L 327, December 22, 2000.
[10] M. MacLeod, D. Mackay, Chemosphere 38 (1999) 1777.
[11] M.N. Sarrion, F.J. Santos, M.T. Galceran, Rapid Commun. Mass Spectrom. 14 (2000) 2271.
[12] B.G. Oliver, K.D. Bothen, Anal. Chem. 52 (1980) 2066.
[13] R.G. Melcher, P.L. Morabito, Anal. Chem. 62 (1990) 2183.
[14] Y. Wang, H.K. Lee, J. Chromatogr. A 803 (1998) 219.
[15] R. Barro, S. Ares, C. Garcia-Jares, M. Llompart, R. Cela, J. Chromatogr. A 1045 (2004) 189.
[16] Y. He, Y. Wang, H.K. Lee, J. Chromatogr. A 874 (2000) 149.
[17] L. Vidal, A. Canals, N. Kalogerakis, E. Psillakis, J. Chromatogr. A 1089 (2005) 25.
[18] H. Zhao, S. Xia, P. Ma, J. Chem. Technol. Biotechnol. 80 (2005) 1089.
[19] J.-F. Peng, J.-F. Liu, G.-B. Jiang, C. Tai, M.-J. Huang, J. Chromatogr. A 1072 (2005) 3.
[20] R.H. Myers, D.C. Montgomery, Response Surface Methodology, Wiley, New York, 2002.
[21] F. Reche, M. Garrigós, M. Marín, A. Cantó, A. Jiménez, J. Chromatogr. A 963 (2002) 419.
[22] I. Arambarri, M. Lasa, R. García, E. Millán, J. Chromatogr. A 1033 (2004) 193.
[23] A. Przyjazny, J.M. Kokosa, J. Chromatogr. A 977 (2002) 143.
[24] S. Shariati-Feizabadi, Y. Yamini, N. Bahramifar, Anal. Chim. Acta 489 (2003) 21.
[25] A.L. Theis, A.J. Waldadack, S.M. Hansen, M.A. Jeannot, Anal. Chem. 73 (2001) 5651.
[26] R. Rodil, A. Carro, R. Lorenzo, M. Abuín, R. Cela, J. Chromatogr. A 963 (2002) 313.
[27] F. Pellati, S. Benvenuti, F. Yoshizaki, D. Bertelli, M. Rossi, J. Chromatogr. A 1087 (2005) 265.
[28] R. Castro, R. Natera, M. García, C. García, J. Chromatogr. A 953 (2002) 7.
[29] P. Diaz, F.J. Señoráns, G. Reglero, E. Ibáñez, J. Agric. Food Chem. 50 (2002) 6468.
[30] F. Piazza, A. Barbieri, F.S. Violante, A. Roda, Chemosphere 44 (2001) 539.
[31] J.C. Flórez, M.L. Fernández, J.E. Sánchez, E. Fernández, A. Sanz-Medel, Anal. Chim. Acta 415 (2000) 9.
[32] E. Psillakis, N. Kalogerakis, J. Chromatogr. A 907 (2001) 211.
[33] Y. Yamini, M. Hojjati, M. Haji-Hosseini, M. Shamsipur, Talanta 62 (2004) 265.
[34] R.-S. Zhao, W.-J. Lao, X.-B. Xu, Talanta 62 (2004) 751.
[35] J.-F. Liu, N. Li, G.-B. Jiang, J.-M. Liu, J. Jönsson, M.-J. Wen, J. Chromatogr. A 1066 (2005) 27.
[36] M. Khajeh, Y. Yamini, J. Hassan, Talanta 69 (2006) 1088.
[37] P. Jandera, J. Fischer, B. Prokes, Chromatographia 54 (2001) 581.
[38] J. Lehotay, K. Hromulakova, J. Liq. Chromatogr. Related Technol. 20 (1997) 3193.
[39] C. Pretti, C. Chiappe, D. Pieraccini, M. Gregori, F. Abramo, G. Monni, L. Intorre, Green Chem. 8 (2006) 238.