# Microwave-assisted headspace single-drop microextration of chlorobenzenes from water samples

**ARTICLE** *in* ANALYTICA CHIMICA ACTA · JUNE 2007

Impact Factor: 4.51 · DOI: 10.1016/j.aca.2007.03.066 · Source: PubMed



**5 AUTHORS**, INCLUDING:

Lorena Vidal
University of Alicante
**28** PUBLICATIONS **833** CITATIONS
SEE PROFILE

Nuria Grané
University of Alicante
**5** PUBLICATIONS **211** CITATIONS
SEE PROFILE

Elefteria Psillakis
Technical University of Crete
**84** PUBLICATIONS **3,251** CITATIONS
SEE PROFILE

Antonio Canals
University of Alicante
**111** PUBLICATIONS **2,006** CITATIONS
SEE PROFILE

Available online at www.sciencedirect.com
ScienceDirect
Analytica Chimica Acta 592 (2007) 9–15
ANALYTICA CHIMICA ACTA
www.elsevier.com/locate/aca

# Microwave-assisted headspace single-drop microextration of chlorobenzenes from water samples

Lorena Vidal [a], Claudia E. Domini [a], Nuria Grané [a], Elefteria Psillakis [b], Antonio Canals [a,*]

[a] *Departamento de Química Analítica, Nutrición y Bromatología, Universidad de Alicante, P.O. Box 99, E-03080 Alicante, Spain*
[b] *Department of Environmental Engineering, Technical University of Crete, Polytechneioupolis, GR-73100 Chania, Crete, Greece*

Received 30 January 2007; received in revised form 27 March 2007; accepted 28 March 2007
Available online 4 April 2007

**Abstract**

A one-step and in-situ sample preparation method used for quantifying chlorobenzene compounds in water samples has been developed, coupling microwave and headspace single-drop microextraction (MW-HS-SDME). The chlorobenzenes in water samples were extracted directly onto an ionic liquid single-drop in headspace mode under the aid of microwave radiation. For optimization, a Plackett–Burman screening design was initially used, followed by a mixed-level factorial design. The factors considered were: drop volume, aqueous sample volume, stirring speed, ionic strength, extraction time, ionic liquid type, microwave power and length of the Y-shaped glass-tube. The optimum experimental conditions found from this statistical evaluation were: a 5 μL microdrop of 1-hexyl-3-methylimidazolium hexafluorophosphate exposed for 20 min to the headspace of a 30 mL aqueous sample, irradiated by microwaves at 200 W and placed in a 50 mL spherical flask connected to a 25 cm Y-shaped glass-tube. Under the optimised experimental conditions, the response of a high performance liquid chromatographic system was found to be linear over the range studied and with correlation coefficients ranging between 0.9995 and 0.9999. The method showed a good level of repeatability, with relative standard deviations varying between 2.3 and 8.3% ($n = 5$). Detection limits were found in the low $\mu g\,L^{-1}$ range varying between 0.016 and 0.039 $\mu g\,L^{-1}$. Overall, the performance of the proposed method demonstrated the favourable effect of microwave sample irradiation upon HS-SDME. Finally, recovery studies from different types of environmental water samples revealed that matrix had little effect upon extraction.


*Keywords:* Chlorinated aromatic compounds; Microwave-assisted; Liquid phase microextraction; Ionic liquid; Experimental design; Water analysis; Sample pretreatment

## 1. Introduction

Over the past two decades there have been some major breakthroughs in the area of sample preparation. The new methods that were introduced were specifically developed to provide rapid sample preparation addressing thus many of the challenges related with sample pretreatment. In 1990, Arthur and Pawliszyn developed a new solvent-free extraction technique, termed solid-phase microextraction (SPME), according which target analytes partitioned between the sample matrix and a small amount of extractant phase dispersed on a solid support [1]. SPME rapidly gained the attention of many research groups around the world counting today numerous applications [2,3]. In 1996, the first configuration of solvent microextraction appeared in the literature [4,5] triggering new investigations on sample preparation techniques based on the miniaturization of the traditional liquid–liquid extraction whereby the solvent (acceptor) to aqueous (donor) phase ratio was greatly reduced. A technique that evolved from this approach was single-drop microextraction (SDME). Initially SDME sampling was accomplished using the immersion method, where the extractant phase consisted of a water-immiscible organic solvent microdrop suspended on the tip of a conventional microsyringe, immersed in a water-sample [6–8]. In 2001, the headspace sampling mode (HS-SDME) was introduced enabling extraction/preconcentration of more volatile analytes from the vapours above the sample, avoiding thus interferences from the sample matrix [9,10]. It is well understood that successful HS-SDME relies on the efficient transfer of target analytes from the sample matrix into the headspace and this is commonly done by using conventional external heat sources. However, previous reports investigating the effect of conventional heating upon HS-SDME concluded

* Corresponding author. Tel.: +34 965909790.
*E-mail address:* a.canals@ua.es (A. Canals).

0003-2670/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.aca.2007.03.066

that although the amount of target analytes present in the headspace is increased, partition coefficients between the drop and the headspace decrease, limiting thus extraction [11,12].

The possibility of using microwave (MW) energy for the extraction of pollutants from environmental samples has been investigated over the past decade and new analytical protocols have been developed [13–15]. The heating mechanism of microwave, which can be mainly interpreted by dielectric polarization and conduction, is very different from that of conventional heating. Microwaves directly couple with the species present in the sample matrix leading to an instantaneous localized superheating [14]. MW has been successfully coupled in the past with SPME for the analysis of polychlorinated biphenyls [16], organochlorinated pesticides [17], semi-volatile compounds (including six chlorobenzenes) [18] and polycyclic aromatic hydrocarbons [19] in water samples. This could indicate that microwave heating has the potential to improve HS-SDME sampling for organic compounds. To the best of our knowledge there are no reports dealing with the coupling MW and HS-SDME and used for the determination of environmental pollutants present in water samples. Microwave irradiation and HS-SDME has been successfully used in the past for the extraction of medicines from dry roots using a two-step procedure (microwave heating and subsequent HS-SDME extraction) [20] and volatile compounds from Chinese herbs (simultaneous microwave and HS-SDME) [21].

The main objective of this study was to evaluate for the first time the possibility of using microwave energy to assist the extraction of chlorobenzene priority listed compounds [22–24] from water samples whilst using HS-SDME. To this end a special home-made experimental set up was prepared allowing MW-HS-SDME extraction of target analytes in one-step and in-situ. The system allows to heat the sample-to-headspace step as long as the headspace-to-drop step is not heated. An ionic liquid was used as the acceptor phase and high performance liquid chromatography-photodiode array detector (HPLC-PDA) was used for separation and detection of target analytes. Factors, such as, drop volume, aqueous sample volume, stirring speed, ionic strength, extraction time, ionic liquid type, microwave power and length of the Y-shaped glass-tube were optimized following a two-step multivariate strategy based on experimental design (Plackett–Burman design for screening and a mixed-level factorial design for optimizing the significant factors). The performance of the optimized method was validated and matrix effects upon extraction were evaluated.

## 2. Experimental

### 2.1. Chemicals and "real-world" water samples

Eight chlorobenzene compounds were used in the present studies, namely: 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) all obtained from Riedel-de Haën (Seelze, Germany). The internal standard solution consisted of a methanol solution of 1,4-dibromobenzene (1,4-DBB), the reagent was obtained from 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 liquids (1-butyl-3-methylimidazolium hexafluorophosphate $[C_4MIM][PF_6]$ and 1-hexyl-3-methylimidazolium hexafluorophosphate $[C_6MIM][PF_6]$), were obtained from Merck (Darmstadt, Germany). Sodium chloride from 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.

The recovery studies were carried out using 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 wastewater (Bilbao, Spain) from a municipal wastewater treatment plant. Samples were collected in 250 mL Pyrex borosilicate amber 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.

### 2.2. MW-HS-SDME and HPLC analysis

The microwave oven used in this work was a domestic Samsung M1711N (2450 MHz, Taiwan) with a maximum power of 800 W, which had a hole (18 mm diameter) in the top of the oven. A microwave stirrer from Scienceware, Bel-Art Products (Pequannock, NJ, USA) was used for stirring the samples at 300 rpm during extraction. The proposed MW-HS-SDME system is shown in Fig. 1 and it is similar to the system shown in Fig. 1 on Ref. [17]. Caution: Be aware of microwave leakage. To this end, a general brand microwave leakage detector was used to check the safety aspects.

The SDME device consisted of a 25 μL Hamilton Gastight syringe (Model 1702 Hamilton Bonaduz AG, Bonaduz, Switzerland; length: 5.1 cm, I.D.: 0.015 cm) where a 3 mm long polytetrafluoroethylene (PTFE) tube (I.D.: 0.8-mm; O.D.: 1.6-mm) was fitted to the blunt needle tip, maximising thus the contact area between the drop and the needle tip. All analyses were performed using a 50-mL spherical flask containing 30 mL of sample solution. The flask was connected to a silanized Y-shaped glass-tube (25 cm length, I.D.: 7 mm) one arm of which was connected to a water condenser (temperature, 21 °C) (Fig. 1). For all quantification experiments, aqueous samples were also spiked with a known amount of the internal standard solution. The microsyringe (typically containing 5 μL of the ionic liquid acceptor phase) was clamped above the Y-shaped glass-tube and its needle passed through the septum, a turn-over flange stopper obtained from Saint-Gobain Verneret (Charmy, France), until its tip was 5.5 cm below the surface of septum. The plunger was depressed and the microdrop of the

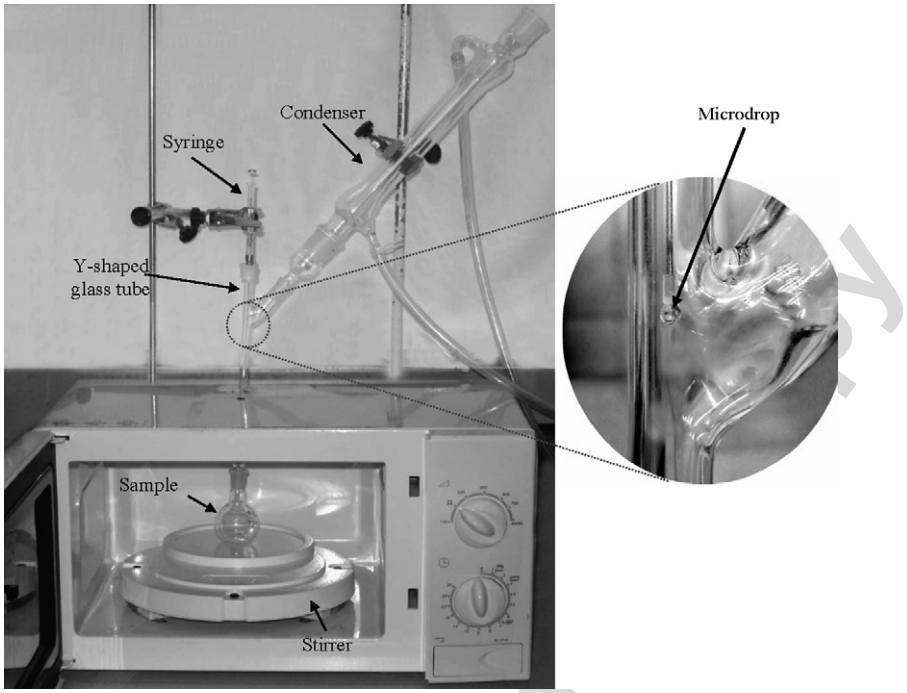


Fig. 1. The assembly of the MW-HS-SDME.

ionic liquid phase was exposed to the headspace of the sample in the Y-shaped glass-tube situated outside the microwave oven. As such, the IL drop was not irradiated when the sample was irradiated at 200 W. It should be mentioned here that in order to avoid a marked increase of the headspace temperature, the sample was initially irradiated for 3 min and then MW energy was applied in the pulse mode in cycles consisting of 30 s "on" followed by 60 s "off". The sampling times examined here were 10, 15 and 20 min corresponding to a 5, 7 and 8.5 min of microwave irradiation time, respectively. After extracting the target analytes the microdrop was retracted into the microsyringe, the PTFE tube was removed and the IL acceptor phase was injected into the HPLC system for analysis following a published procedure [12]. In short, a 7725i Rheodyne injector (Rohnert Park, CA, USA) and a Phenomenex Luna $C_{18}$ column (250 mm × 4.6 mm, 5 μm particle size) were used, respectively, for injection and separation of the target analytes. A Photodiode Array Detector (PDA) set at 210 nm from Waters (Milford, MA, USA) was used for detecting all target analytes. The mobile phase consisted of a 65:35 (v/v) mixture of acetonitrile–water at a 1 mL $min^{-1}$ flowrate. Fig. 1 on Ref. [12] shows a typical chromatogram.

### 2.3. Data handling and processing

According to previous reports, the response of the instrument used in the present studies was based on the sum of the areas of the individual peaks eluting during HPLC-PDA analysis [12,25–27].

Experimental design matrices were constructed and the results were evaluated using the Statgraphics Statistical Computer Package "Statgraphics Plus 5.1".

## 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 [28], which assumes that the interactions can be completely ignored and so the main effects are calculated with a reduced number of experiments. A saturated Plackett–Burman matrix was employed because of the large number of parameters to be tested. A matrix with 11 factors (eight real factors and three fictitious factors or dummy factors) was used. The effects of dummy factors are used for the estimation of the experimental error used in the statistical interpretation [29,30].

Based on the literature and the experience of the laboratories eight real factors were selected to define the experimental field (namely: drop volume, aqueous sample volume, stirring speed, ionic strength, extraction time, ionic liquid type, microwave power and length of the Y-shaped glass-tube) with two levels for each factor. Table 1 gives the examined levels for each factor and matrix design. The latter had 12 runs randomly carried out in order to nullify the effect of extraneous or nuisance factors.

An ANOVA test was used to evaluate the data and statistically significant effects were determined using a *t*-test with a 95% probability [29,30]. Effects were also visualized by drawing normal probability plots for the normalized effects. According to the results, extraction time was the most significant factor having a positive sign. Sample volume followed by ionic liquid

Table 1
Experimental factors, levels and matrix of the Plackett–Burman design

| Factor | Code | Level | |
|---|---|---|---|
| | | Low (−) | High (+) |
| Ionic strength (NaCl concentration; %, w/v) | NaCl | 0 | 30 |
| Drop volume (μL) | *D* | 5 | 8 |
| Sample volume (mL) | *V* | 10 | 30 |
| Extraction time (min) | *t* | 10 | 20 |
| Stirring speed (rpm) | *S* | 0 | 300 |
| Ionic liquid type | IL | $[C_4MIM][PF_6]$ | $[C_6MIM][PF_6]$ |
| Microwave power (W) | *P* | 100 | 200 |
| Y-shaped glass-tube length (cm) | *L* | 25 | 35 |

| Run | NaCl | *D* | *V* | *t* | *S* | IL | *P* | *L* | Dummy 1 | Dummy 2 | Dummy 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | −1 | 1 | 1 | −1 | 1 | −1 | −1 | −1 | 1 | 1 |
| 2 | 1 | 1 | 1 | −1 | 1 | 1 | −1 | 1 | −1 | −1 | −1 |
| 3 | 1 | 1 | −1 | 1 | −1 | −1 | −1 | 1 | 1 | 1 | −1 |
| 4 | −1 | 1 | 1 | −1 | 1 | −1 | −1 | −1 | 1 | 1 | 1 |
| 5 | 1 | −1 | −1 | −1 | 1 | 1 | 1 | −1 | 1 | 1 | −1 |
| 6 | 1 | −1 | 1 | −1 | −1 | −1 | 1 | 1 | 1 | −1 | 1 |
| 7 | −1 | −1 | −1 | 1 | 1 | 1 | −1 | 1 | 1 | −1 | 1 |
| 8 | −1 | 1 | 1 | 1 | −1 | 1 | 1 | −1 | 1 | −1 | −1 |
| 9 | 1 | 1 | −1 | 1 | 1 | −1 | 1 | −1 | −1 | −1 | 1 |
| 10 | −1 | −1 | 1 | 1 | 1 | −1 | 1 | 1 | −1 | 1 | −1 |
| 11 | −1 | 1 | −1 | −1 | −1 | 1 | 1 | 1 | −1 | 1 | 1 |
| 12 | −1 | −1 | −1 | −1 | −1 | −1 | −1 | −1 | −1 | −1 | −1 |

type were the next most significant factors showing a positive sign. Interestingly, microwave power appeared to have a positive yet non-significant effect upon extraction. A possible explanation for this positive behaviour might be the fact that at 200 W, microwave radiation is applied for longer times enhancing thus mass transfer from the aqueous sample to the headspace. As expected drop volume showed a negative, yet, non-significant effect. This is in agreement with previously published results [9,12,31–33] and it 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 [9]. In addition, stirring speed appeared to have a negative non-significant effect. This is most probably due to the fact that the maximum agitation speed that could be applied here was 300 rpm a relatively low value with possibly negligible effect upon extraction. As expected, the Y-shaped glass-tube length appears to have a negative non-significant effect upon extraction. Increasing the length of the glass-tube results in an increase of the headspace volume, reducing thus the total amount of target analytes that can be extracted. Ionic strength also shows a negative non-significant effect and this observation is in agreement with previously published results [12,16,34] and it could be attributed to the existence of a negative interaction between temperature and sodium chloride [12] that produce a negative effect upon extraction. Overall, the results of this first screening study revealed that five factors could be fixed (namely: 200 W microwave power, 5 μL ionic liquid drop volume; 25 cm Y-shaped glass-tube length, no agitation or addition of NaCl) for the following optimization step.

### 3.2. Optimization design

Next, a factorial design was carried out to assess the influence of the three main factors on the microwave-microextraction process in order to obtain the optimal working conditions. Given that one of the main factors considered was limited at two levels and the other two were able to work at three levels, a mixed-level factorial design was used. This type of experimental design consists of all level combination of two or more factors, where the user sets the number of levels. In our case, the general mixed-level factorial design is $\{2^k \times 3^{k'}\}$, where the exponents represent the number of factors for each level and the bases stand for the levels of each factor in the experiments [35–37]. The factors included in the factorial design were: Ionic liquid type, at two levels ($[C_4MIM][PF_6]$ and $[C_6MIM][PF_6]$), extraction time at three levels (10, 15 and 20 min) and sample volume at three levels (10, 20 and 30 mL) (Table 2). The overall design, expressed as $\{2^1 \times 3^2\}$, involved 36 runs (18 runs in duplicate).

The data obtained were evaluated by ANOVA test and the effects were visualized using Pareto chart shown in Fig. 2. As can be seen, sample volume and extraction time were the most significant factors, both exhibiting a positive effect, whilst the type of ionic liquid was found to have a non-significant positive effect. A closer examination of the interaction between two factors revealed that the interaction between sample volume and extraction time (denoted as AB in Fig. 2) was statistically significant, showing a positive effect upon extraction.

Furthermore, plotting the instrumental response as a function of all the factors controlling the extraction process enabled visualisation of the separate effects of pairs of factors. The resulting

Table 2
Experimental factors, levels and matrix of the mixed-level factorial design

| Factor | Code | Level | | |
|---|---|---|---|---|
| | | Lower (−) | Central (0) | Upper (+) |
| Sample volume (mL) | $V$ | 10 | 20 | 30 |
| Extraction time (min) | $t$ | 10 | 15 | 20 |
| Ionic liquid type | IL | $[C_4MIM][PF_6]$ | – | $[C_6MIM][PF_6]$ |

| Run | $V$ | $t$ | IL |
|---|---|---|---|
| 1 | 1 | 0 | −1 |
| 2 | −1 | 1 | 1 |
| 3 | 0 | 1 | −1 |
| 4 | 1 | −1 | 1 |
| 5 | −1 | −1 | 1 |
| 6 | 0 | 0 | −1 |
| 7 | 1 | −1 | −1 |
| 8 | 1 | 1 | −1 |
| 9 | 0 | 0 | 1 |
| 10 | −1 | −1 | −1 |
| 11 | 0 | 1 | 1 |
| 12 | −1 | 1 | −1 |
| 13 | 1 | 0 | 1 |
| 14 | −1 | 0 | 1 |
| 15 | 1 | 1 | 1 |
| 16 | 0 | −1 | 1 |
| 17 | 0 | −1 | −1 |
| 18 | −1 | 0 | −1 |

plots are given in Fig. 3 where the instrument's response surface is obtained by plotting sample volume versus extraction time ($[C_6MIM][PF_6]$ as extractant) (Fig. 3a), sample volume versus ionic liquid type (extraction time of 15 min) (Fig. 3b), and extraction time versus ionic liquid type (20 mL sample volume) (Fig. 3c). As can be seen, sample volume shows a clear positive effect upon extraction (Fig. 3a and b), reaching a maximum at 30 mL. As expected, increasing the aqueous sample volume appears to be beneficial for the instrument's signal, given that the total amount of analytes present in the reduced headspace is increased. Extraction time also shows a positive effect upon extraction (Fig. 3a and c), reaching a maximum at 20 min. Indeed, increasing the extraction time and as a consequence the irradiation time leads to an increase of the total amount of analytes present in the headspace. Finally, the type of ionic liquid shows a non-significant positive effect (Fig. 3b and c) and this observation is in agreement with previously published results [38].

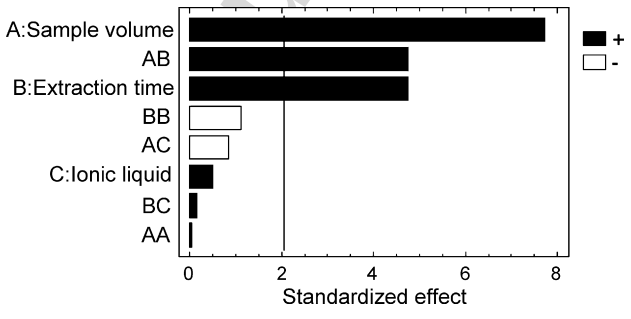


Fig. 2. Pareto chart of the three main factors in the mixed-level factorial design.

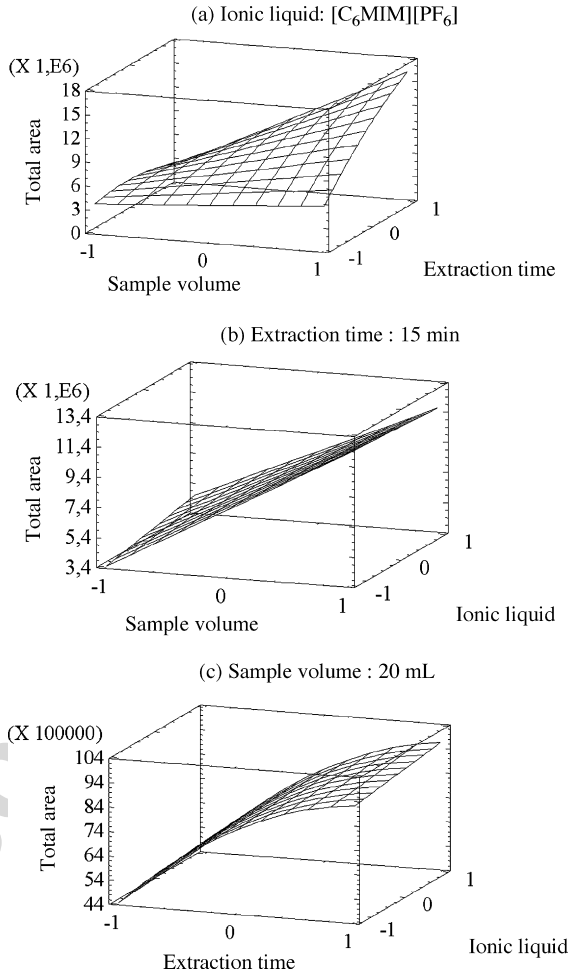


Fig. 3. Response surfaces for total chromatographic peak area using the mixed-level factorial design obtained by plotting: (a) sample volume vs. extraction time (ionic liquid: $[C_6MIM][PF_6]$); (b) sample volume vs. ionic liquid type (extraction time: 15 min); and (c) extraction time vs. ionic liquid type (sample volume: 20 mL).

The results of this second optimization study revealed that the response of the analytical instrument is expected to be maximized when using a 30 mL sample volume, a 20 min extraction time and with $[C_6MIM][PF_6]$ as the acceptor phase. Overall, the results of the two steps yielded the following optimum experimental conditions: 30 mL sample volume; 20 min extraction time; $[C_6MIM][PF_6]$ as ionic liquid; 200 W microwave power; 5 μL ionic liquid drop volume; 25 cm Y-shaped glass-tube length, and no agitation or addition of NaCl.

### 3.3. Validation of MW-HS-SDME

The optimum MW-HS-SDME conditions were then used to test the applicability of the proposed method for quantitative determination of target analytes. A calibration study was performed by spiking pure water with analytes over the concentration range of 1–320 $\mu g\,L^{-1}$. The calculated calibration curves gave a high level of linearity for all target analytes with correlation coefficients ($r$) ranging between 0.9995 and 0.9999 as shown in Table 3. The repeatability of the proposed method,

Table 3
Main method parameters for the extraction of chlorobenzenes from water samples using the optimized microwave-assisted headspace SDME method

| Analyte | Slope ± S.D. | Intercept ± S.D. | Correlation coefficient ($r$)[a] | R.S.D. (%)[b] | LOD ($\mu g\,L^{-1}$)[c] | LOQ ($\mu g\,L^{-1}$)[d] |
|---|---|---|---|---|---|---|
| 1,2-DCB | 0.1075 ± 0.0008 | 0.1 ± 0.1 | 0.9998 | 2.7 | 0.024 | 0.081 |
| 1,4-DCB | 0.0669 ± 0.0005 | −0.03 ± 0.07 | 0.9998 | 2.3 | 0.039 | 0.130 |
| 1,3-DCB | 0.0951 ± 0.0003 | −0.04 ± 0.04 | 0.9999 | 2.9 | 0.032 | 0.108 |
| 1,2,3-TCB | 0.199 ± 0.002 | −0.4 ± 0.2 | 0.9998 | 5.7 | 0.016 | 0.054 |
| 1,2,4-TCB | 0.168 ± 0.003 | 0.2 ± 0.4 | 0.9995 | 5.6 | 0.022 | 0.072 |
| 1,3,5-TCB | 0.218 ± 0.002 | −0.2 ± 0.2 | 0.9998 | 3.8 | 0.022 | 0.072 |
| 1,2,3,4-TeCB | 0.268 ± 0.002 | −0.3 ± 0.2 | 0.9998 | 8.3 | 0.016 | 0.054 |
| 1,2,4,5-TeCB | 0.361 ± 0.004 | 0.8 ± 0.5 | 0.9996 | 7.1 | 0.016 | 0.054 |

[a] Linear range: 1–320 $\mu g\,L^{-1}$ (number of calibration points = 9).
[b] Relative standard deviation (R.S.D.); mean value for five replicate analyses; spiking level 40 $\mu g\,L^{-1}$.
[c] Limits of detection (LODs) were calculated for a three signal-to-noise ratio (S/N = 3).
[d] Limits of quantification (LOQs) were calculated for a ten signal-to-noise ratio (S/N = 10).

expressed as relative standard deviation (R.S.D.), was evaluated by extracting five consecutive aqueous samples (spiked at 40 $\mu g\,L^{-1}$ with each target analyte) and was found to vary between 2.3 and 8.3% with a mean value of 4.8% (Table 3). 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 ten 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 0.016 and 0.039 $\mu g\,L^{-1}$ and between 0.054 and 0.130 $\mu g\,L^{-1}$, respectively. It should be mentioned here, that these values are considerably lower than the ones previously reported for HPLC analysis of chlorobenzenes in water samples [12,39,40]. In particular when the same HS-SDME approach is adopted without heating, LODs and LOQs were found to range between 0.102 and 0.203 $\mu g\,L^{-1}$ and between 0.338 and 0.677 $\mu g\,L^{-1}$, respectively [12]. This clearly demonstrates the favourable effect of microwave heating upon HS-SDME.

In order to investigate the effect of sample matrix upon the MW-HS-SDME procedure five replicate analyses of different types of "real-world" water samples (namely tap water, river water and effluent wastewater) were spiked at 40 $\mu g\,L^{-1}$ with each target contaminant and were analysed under the optimized experimental conditions. It should be mentioned here that none of these selected samples showed initial detectable concentration of the target compounds. Relative recoveries were determined as the ratio of the concentrations found in real and deionised water samples spiked at the same contamination level [12]. The results for each set of experiments, summarised in Table 4, show that for the tap water samples relative recoveries ranged between 91 and 104%, with a mean value of 99%, for the river water samples between 98 and 106%, with a mean value of 101%, and for effluent wastewater samples between 82 and 99%, with a mean value of 89%. This is in agreement with our previous investigations on the recovery studies using no heated HS-SDME where the relatively elevated R.S.D. values as well as decreased relative recoveries observed in the case of the effluent wastewater matrix were attributed to possible competitive adsorption of target analytes to suspended solids reducing thus the effective concentration of pollutants in the aqueous phase. Nevertheless, the matrix effect in the effluent wastewater has been reduced for the more hydrophobic target pollutants (namely: 1,2,3,4-tetrachlorobenzene and 1,2,4,5-tetrachlorobenzene) [12].

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

| Analyte | Relative recoveries (%) and R.S.D. values (%) in parentheses[a] | | |
|---|---|---|---|
| | Tap water | River water | Effluent wastewater |
| 1,2-DCB | 96.2 (1.8) | 100.9 (4.0) | 88.6 (7.4) |
| 1,4-DCB | 91.4 (5.2) | 98.1 (5.9) | 83.7 (11.3) |
| 1,3-DCB | 96.2 (3.7) | 99.0 (5.9) | 82.9 (12.0) |
| 1,2,3-TCB | 100.1 (2.1) | 99.7 (2.3) | 94.9 (1.7) |
| 1,2,4-TCB | 103.9 (5.6) | 101.4 (3.3) | 90.8 (5.0) |
| 1,3,5-TCB | 101.3 (5.8) | 99.7 (4.1) | 81.7 (11.7) |
| 1,2,3,4-TeCB | 102.5 (4.4) | 105.5 (6.1) | 98.9 (4.4) |
| 1,2,4,5-TeCB | 101.7 (3.4) | 100.2 (3.0) | 93.3 (1.8) |

[a] Five replicate analyses at a 40 $\mu g\,L^{-1}$ spiking level.

## 4. Conclusions

A one-step microwave-assisted headspace single-drop microextraction procedure has been developed to extract chlorobenzenes from water samples. The new method combines synergistically the advantages of headspace single-drop microextraction (i.e., miniaturization), ionic liquid as extractant (i.e., environmentally friendly and low vapour pressure) and microwave heating (i.e., speed). The favourable effect of microwave upon headspace single-drop microextration has been demonstrated and the results indicate that this extraction procedure is efficient, sensitive and precise exhibiting better extraction efficiency when compared to the previous no heated HS-SDME [12].

## Acknowledgements

The authors would like to thank the Spanish Ministry of Education and Science (projects n. PTR1995-0882-OP-02-01, CTQ2005-09079-C03-01/BQU and CAL03-078-C3-2) for the financial support of this work. This work has been undertaken as part of the EU sponsored COST programme (Action D32,

working group D32/005/04, "Microwaves and Ultrasound Activation in Chemical Analysis"). L.V. also thanks "Vicerrectorado de Investigación, Desarrollo e Innovación" of University of Alicante for her scholarship.

## References

[1] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[2] H. Lord, J. Pawliszyn, J. Chromatogr. A 885 (2000) 153.
[3] C. Dietz, J. Sanz, C. Cámara, J. Chromatogr. A 1103 (2006) 183.
[4] H. Liu, P.K. Dasgupta, Anal. Chem. 68 (1996) 1817.
[5] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 68 (1996) 2236.
[6] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 69 (1997) 235.
[7] Y. He, H.K. Lee, Anal. Chem. 69 (1997) 4634.
[8] E. Psillakis, N. Kalogerakis, TrAC Trends Anal. Chem. 21 (2002) 53.
[9] A.L. Theis, A.J. Waldack, S.M. Hansen, M.A. Jeannot, Anal. Chem. 73 (2001) 5651.
[10] A. Tankeviciute, R. Kazlauskas, V. Vickackaite, Analyst 126 (2001) 1674.
[11] J.-F. Liu, N. Li, G.-B. Jiang, J.-M. Liu, J. Jönsson, M.-J. Wen, J. Chromatogr. A 1066 (2005) 27.
[12] L. Vidal, E. Psillakis, C. Domini, N. Grané, F. Marken, A. Canals, Anal. Chim. Acta 584 (2007) 189.
[13] F. Smith, G. Xiong, The use of microwave-assisted techniques for samples preparation in environmental organic analysis, in: R.A. Meyers (Ed.), Encyclopedia of Analytical Chemistry, Wiley, Chichester, UK, 2000.
[14] C.S. Eskilsson, E. Björklund, J. Chromatogr. A 902 (2000) 227.
[15] V. Camel, TrAC Trends Anal. Chem. 19 (2000) 229.
[16] Y.Y. Shu, S.S. Wang, M. Tardif, Y. Huang, J. Chromatogr. A 1008 (2003) 1.
[17] H.-P. Li, G.-C. Li, J.-F. Jen, J. Chromatogr. A 1012 (2003) 129.
[18] Y. Huang, Y.-C. Yang, Y.Y. Shu, J. Chromatogr. A 1140 (2007) 35.
[19] M.-C. Wei, J.-F. Jen, Talanta, doi:10.1016/j.talanta.2007.01.017.
[20] C. Deng, Y. Mao, F. Hu, X. Zhang, J. Chromatogr. A 1103 (2006) 15.
[21] C. Deng, Y. Mao, F. Hu, X. Zhang, J. Chromatogr. A, doi:10.1016/j.chroma.2006.08.074.
[22] World Health Organisation (WHO), 10th Report on Carcinogens, National Toxicology Program, Public Health Service, 2002.
[23] 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, 18 May 1976.
[24] 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, 22 December 2000.
[25] F. Pellati, S. Benvenuti, F. Yoshizaki, D. Bertelli, M. Rossi, J. Chromatogr. A 1087 (2005) 265.
[26] R. Castro, R. Natera, M. García, C. García, J. Chromatogr. A 953 (2002) 7.
[27] P. Diaz, F.J. Señoráns, G. Reglero, E. Ibáñez, J. Agric. Food Chem. 50 (2002) 6468.
[28] R.H. Myers, D.C. Montgomery, Response Surface Methodology, Wiley, New York, 2002.
[29] H. Fabre, N. Mesplet, J. Chromatogr. A 897 (2000) 329.
[30] Y.V. Heyden, C. Hartmann, D.L. Massart, L. Michel, P. Kiechle, F. Erni, Anal. Chim. Acta 316 (1995) 15.
[31] L. Vidal, A. Canals, N. Kalogerakis, E. Psillakis, J. Chromatogr. A 1089 (2005) 25.
[32] A. Przyjazny, J.M. Kokosa, J. Chromatogr. A 977 (2002) 143.
[33] S. Shariati-Feizabadi, Y. Yamini, N. Bahramifar, Anal. Chim. Acta 489 (2003) 21.
[34] Y.-I. Chen, Y.-S. Su, J.-F. Jen, J. Chromatogr. A 976 (2002) 349.
[35] D.C. Montgomery, Design and Analysis of Experiments, Wiley, New York, 2005.
[36] J. Lamas, C. Salgado, C. García, M. Llompart, R. Cela, M. Gómez, J. Chromatogr. A 1046 (2004) 241.
[37] V. Casas, M. Llompart, C. García, R. Cela, T. Dagnac, J. Chromatogr. A 1124 (2006) 148.
[38] J.-F. Liu, G.-B. Jiang, Y.-G. Chi, Y.-Q. Cai, Q.-X. Zhou, J.-T. Hu, Anal. Chem. 75 (2003) 5870.
[39] P. Jandera, J. Fischer, B. Prokes, Chromatographia 54 (2001) 581.
[40] J. Lehotay, K. Hromulakova, J. Liq. Chromatogr. Related Technol. 20 (1997) 3193.