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Headspace single-drop microextraction for the analysis of chlorobenzenes in water samples

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Abstract

Exposing a microlitre organic solvent drop to the headspace of an aqueous sample contaminated with ten chlorobenzene compounds proved to be an excellent preconcentration method for headspace analysis by gas chromatography–mass spectrometry (GC–MS). The proposed headspace single-drop microextraction (SDME) method was initially optimised and the optimum experimental conditions found were: 2.5 μl toluene microdrop exposed for 5 min to the headspace of a 10 ml aqueous sample containing 30% (w/v) NaCl placed in 15 ml vial and stirred at 1000 rpm. The calculated calibration curves gave a high level of linearity for all target analytes with correlation coefficients ranging between 0.9901 and 0.9971, except for hexachlorobenzene where the correlation coefficient was found to be 0.9886. The repeatability of the proposed method, expressed as relative standard deviation varied between 2.1 and 13.2% ($n = 5$). The limits of detection ranged between 0.003 and 0.031 μg/l using GC–MS with selective ion monitoring. Analysis of spiked tap and well water samples revealed that matrix had little effect on extraction. A comparative study was performed between the proposed method, headspace solid-phase microextraction (SPME), solid-phase extraction (SPE) and EPA method 8121. Overall, headspace SDME proved to be a rapid, simple and sensitive technique for the analysis of chlorobenzenes in water samples, representing an excellent alternative to traditional and other, recently introduced, methods.

Keywords: Chlorinated benzenes; Headspace SDME; Solvent microextraction; Water analysis

1. Introduction

Chlorobenzenes are a class of environmental pollutants used as industrial solvents, pesticides, dielectric fluids, deodorant and chemical intermediates. Their presence in the environment is a result of uncontrolled release of solid/liquid effluents as well as industrial atmospheric discharges [1]. It is well known that once chlorobenzenes enter the aquatic environment they tend to accumulate on living organisms [2]. This is of great concern given that chlorobenzenes feature prominently within several listings of priority hazardous substances due to their acute toxicity. Hexachlorobenzene and 1,4-dichlorobenzene were the first compounds included in the Third and Fifth (respectively) Annual Report on Carcinogens in the US Department of Health and Human Services as reasonably anticipated to be a human carcinogens based on sufficient evidence of carcinogenicity in experimental animals [3]. A number of chlorobenzene compounds are also included in the Council Directive 76/464/EEC [4] on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community, and under the Water Framework Directive 2000/60/EC [5]. In light of this, research is directed towards developing inexpensive, simple and efficient sample preparation and analytical techniques for the detection of trace quantities of these compounds in water samples.

In general, liquid–liquid extraction (LLE) [6,7] and solid-phase extraction (SPE) [8,9] are the most commonly used sample pretreatment methods for the isolation and/or enrichment of chlorobenzenes. An alternative preconcentration method for aqueous samples is solid-phase microextraction

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(SPME), according which, analytes partition between the stationary phase on a SPME fibre and the sample until equilibrium is achieved [10]. In SPME, there are two main types of SPME sampling: immersion sampling where the fibre is immersed into the aqueous solution and headspace sampling where the fibre is exposed to the headspace above the liquid (or solid) sample [11]. Immersion sampling is widespread in the SPME approach but for volatile compounds and dirty samples the headspace mode is preferred as it results into faster equilibration times and higher selectivity. Regarding the analysis of chlorobenzenes in water samples the headspace sampling mode has been previously reported [12], although immersion SPME has been used for the determination of fibre-water distribution constants [13] and testing a recently proposed semi-empirical model [14].

An attractive alternative to traditional and recently introduced extraction techniques is solvent microextraction, which is based on the miniaturisation of the traditional liquid–liquid extraction method, by greatly reducing the solvent to aqueous ratio. Single-drop microextraction (SDME) evolved from this approach where the extractant phase is a drop of a water-immiscible solvent suspended in the aqueous sample [15]. In 2001, the possibility of using a hanging microlitre solvent drop (headspace SDME) to achieve preconcentration in headspace analysis of volatile organic compounds (VOC) in an aqueous matrix was reported for the first time [16,17]. There are very few reports dealing with this new preconcentration methodology, which represents an emerging field of study due to the inherent advantages of being fast, inexpensive, precise and virtually solventless [18–25].

The objective of the present work is to investigate for the first time, the possibility of using headspace SDME for the analysis of ten chlorobenzenes in water samples. The proposed method was optimized by controlling parameters such as extraction solvent, drop volume, headspace/aqueous sample volume, agitation speed, ionic strength and sampling time. The performance of the developed protocol was evaluated and compared to that of other extraction methods.

2. Experimental

2.1. Chemicals and aqueous samples

The ten chlorobenzene compounds considered in this work were: 1,3-dichlorobenzene (1,3-DCB), 1,4-dichlorobenzene (1,4-DCB), 1,2-dichlorobenzene (1,2-DCB), 1,3,5-trichlorobenzene (1,3,5-TCB), 1,2,4-trichlorobenzene (1,2,4-TCB), 1,2,3-trichlorobenzene (1,2,3-TCB), 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), pentachlorobenzene (PCB) and hexachlorobenzene (HCB) were obtained from Riedel-de Haën (Seelze, Germany). A toluene solution of 1,4-dibromobenzene (1,4-DBB) (Riedel-de Haën, Seelze, Germany) was prepared and used as the internal standard solution. All organic solvents (namely toluene, *n*-hexane, *n*-heptane, methanol and acetonitrile) were of pesticide grade and were also obtained from Riedel-de Haën (Seelze, Germany). Deionised water was prepared on a water purification system (EASYpure® RF) supplied by Barnstead/Thermolyne Corporation (Dubuque, IO, USA).

Standard stock solutions of 500 mg/l of target compounds were prepared in acetonitrile/methanol (50/50, v/v). All solutions were stored in the dark at 4 °C. Working solutions were prepared by dilution of standard stock solutions with deionised water. Sodium chloride (Merck, Darmstadt, Germany) was used to adjust the ionic strength of the aqueous samples.

Recovery studies were carried out using tap water obtained from the main area water-supply network of Chania (Greece) and well water obtained from a well in the Monastery of Agia Triada, in the Kounoupidiana area, Chania. Preliminary analyses on tap water and well water samples under the full-scan and selective ion monitoring (SIM) mass spectrometry modes ensured that they were free of all target analytes. All samples were collected in 250 ml Pyrex borosilicate amber glass containers with caps, lined with aluminium foil. They were stored in the dark at 4 °C and were analysed without previous treatment or filtration within 48 h of collection. Before extraction, the ionic strength of the water samples was adjusted to the one required by the extraction method used.

2.2. Headspace SDME

Unless otherwise stated within the text, for headspace SDME, 10 ml of a salted (30%, w/v NaCl) aqueous solution spiked at a known concentration with all target analytes, was placed in a 15 ml crimp top glass vial containing a glass coated stirring bar and fitted with a Mininert Valve (Supelco, Bellefonte, PA, USA). Magnetic stirring (typically 1000 rpm i.e. 90% of the stirrer's maximum speed) was applied before (allowing thus equilibrium to be attained between the aqueous and gaseous phases) and during extraction. It should be mentioned here, that in order to eliminate volatilisation losses, all aqueous samples were freshly prepared before each headspace SDME extraction.

A 10 μl Hamilton Gastight syringe (Hamilton Bonaduz AG, Bonaduz, Switzerland), Model 1701, with a bevel needle tip (length: 5.1 cm, i.d.: 0.013 cm, bevel 22°), typically containing 2.5 μl of the appropriate organic solvent was clamped above the vial containing the water sample. For all quantification experiments, 2.5 μl of toluene solution spiked with a 10 mg/l of the internal standard was used instead. The microsyringe was then lowered and its needle passed through the Mininert valve until the tip of the needle was 1 cm below the lower surface of valve. The plunger was depressed and the 2.5-μl drop of the organic phase was exposed to the headspace above the sample. The analytes were then allowed to partition between the headspace and the organic phase at room temperature (22 °C; air-conditioned) for 5 min (unless otherwise stated within the text). After extraction, 1.2 μl of solvent were retracted into the microsyringe and transferred to the heated

injection port of the gas chromatograph–mass spectrometer (GC–MS) for analysis.

2.3. GC–MS analysis

All analyses were carried-out on a Shimadzu GC-17A, Version 3, QP-5050A Gas Chromatograph/Mass Spectrometer system (Shimadzu Corporation, Kyoto, Japan) equipped with a 30 m × 0.25 mm 0.25 μm HP-5MS capillary column (Agilent Technologies). The injector was maintained at 200 °C and operated in the splitless mode with the split closed for 5 min. Helium (>99.999% pure) was used as the carrier gas at a flow-rate of 1.2 ml/min. The column oven was initially set at 40 °C for 4 min, programmed to 130 °C at a 5 °C/min rate, and finally to 220 °C at 10 °C/min rate, where it was held for 2 min. The interface temperature was set at 240 °C and the detector voltage at 1.50 kV. A 10 min solvent cut time was allowed for all analyses. The ionization mode was electron impact (70 eV). A SIM program was constructed for GC–MS acquisition and quantification. Acquisition of data was divided in five ion sets (each one having specific ions for the compounds eluting at this time frame) with acquisition starting at 11.50 min for ion set 1, 15.00 min for ion set 2, 20.00 min for ion set 3, 25.00 min ion set 4 and finally 28.00 min for ion set 5. The base peak ion of each analyte was chosen as the quantifying ion and two other significant ions were selected as qualifying ions. Overall, quantification was based on the following target ions (*m/z*) 1,3-DCB: 146, 1,4-DCB: 146, 1,2-DCB: 146, 1,3,5-TCB: 180, 1,2,4-TCB: 180, 1,4-DBB: 236 (internal standard), 1,2,3-TCB: 180, 1,2,4,5-TeCB: 216, 1,2,3,4-TeCB: 216, PCB: 250 and HCB: 284. Prior to quantification in the SIM mode, the full scan mode (*m/z* 40–350) was used for identification of all target compounds based on their mass spectra and GC retention times.

3. Results and discussion

3.1. Optimisation of headspace SDME

The first step in the optimisation procedure was to select an appropriate extraction solvent. Accordingly, high-purity toluene, *n*-hexane and *n*-heptane were tested as potential acceptor phases. Solvent selectivity was evaluated after exposing for 5 min 3-μl organic solvent drop to the headspace of a 15 ml glass vial containing 10 ml deionised water samples, stirred at 1000 rpm and spiked at 50 μg/l with all target analytes. From the three tested solvents, *n*-hexane had the tendency to evaporate in faster rates once exposed to the air, most probably due to the fact that it had the higher vapour pressure (20131.7 Pa) when compared to the others. *n*-Heptane was found to be more resistant to evaporation due to its lower vapour pressure (6132.8 Pa) and resulted in enhanced extraction of target analytes when compared to *n*-hexane. Overall, toluene gave the best results by combining the highest extraction efficiency as well as having the lowest vapour pressure (3786.4 Pa). Toluene has been successfully used in the past for the dynamic headspace liquid-phase microextraction of five chlorobenzene compounds (1,3,5-TCB, 1,2,3,4-TeCB, 1,2,4,5-TeCB, PCB and HCB) from soil samples, where the microsyringe barrel is used as a separatory funnel, featuring the repeated movement of the syringe plunger [25]. It should be mentioned here that although octanol is commonly employed in headspace SDME, the possibility of using this extraction solvent was not investigated given that its solvent peak was found to interfere with the target eluting analytes [25].

In a separate set of experiments, the effect of the organic drop volume was investigated. Accordingly, toluene drop volumes of 2, 2.5 and 3 μl were exposed separately for 5 min at 22 °C (air-conditioned) to the headspace of 10 ml aqueous solution spiked at 50 μg/l with all target analytes and stirred at 1000 rpm. As expected, increasing the organic drop volume from 2 to 2.5 μl, resulted in an increase of the extraction efficiency. However, a further increase of the toluene drop from 2.5 μl to 3 μl decreased extraction and the resulting analytical signal was approximately the same as for the 2 μl toluene drop. This is not the first time that such a trend in extraction is observed while investigating the effect of the organic drop volume [18,20]. For example, a recent report investigated headspace SDME analysis of polycyclic aromatic hydrocarbons in 6 ml water samples, after exposing for 12 min in the sample-headspace 1-butanol drop volumes up to 3.5 μl [20]. The authors reported that increasing the drop volume up to 3 μl, resulted in enhanced extraction efficiency. However, the 3.5 μl 1-butanol drop resulted in decreased response of the analytical instrument and the authors concluded that the unfavourable effect of larger organic drop volumes is attributed to insufficient equilibration time [18,20]. In general, diffusion coefficients in the gas phase are much larger than the corresponding diffusion coefficients in condensed phases and as such mass transfer in the headspace is assumed to be a fast process [16]. Furthermore, during headspace SDME, headspace convection is induced due to stirring of the aqueous phase. Nonetheless, the microdrop is expected to be stagnant and consequently mass transfer into the drop is by diffusion alone, representing thus a slow step in the overall extraction procedure and explaining the extended equilibration times needed for larger organic solvent drops [16]. Based on these considerations, it was decided to use a 2.5 μl toluene drop for all subsequent experiments.

In order to evaluate the effect of aqueous sample volume upon extraction, additional experiments were performed using 15 ml vials containing sample volumes ranging from 5 to 10 ml. For these experiments, the variation of the analytical response of the instrument was monitored after exposing 2.5-μl toluene drops for 5 min at 22 °C (air-conditioned) to the headspace of 5, 7 and 10 ml aqueous solutions each one spiked at 50 μg/l with all target analytes and stirred at 1000 rpm. As expected, increasing the aqueous sample volume resulted in a net increase of the analytical signal [15], given that the total amount of analytes present in the solution

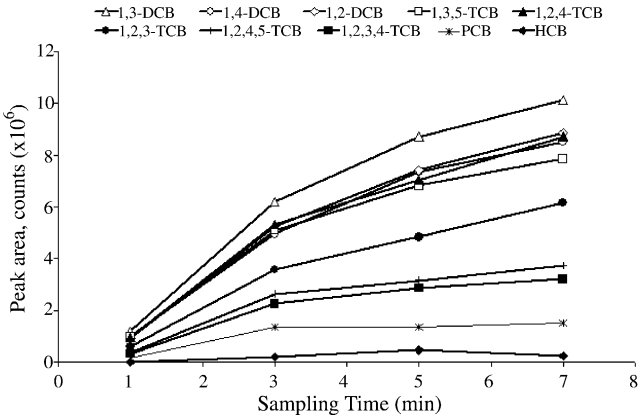

Fig. 1. Effect of sampling time on the extraction efficiency of headspace SDME used for the analysis of chlorobenzenes in water samples. Other experimental conditions: 50 μg/l concentration level; 10 ml aqueous sample in 15 ml glass vial; 2.5 μl toluene drop volume; 1000 rpm stirring rate.

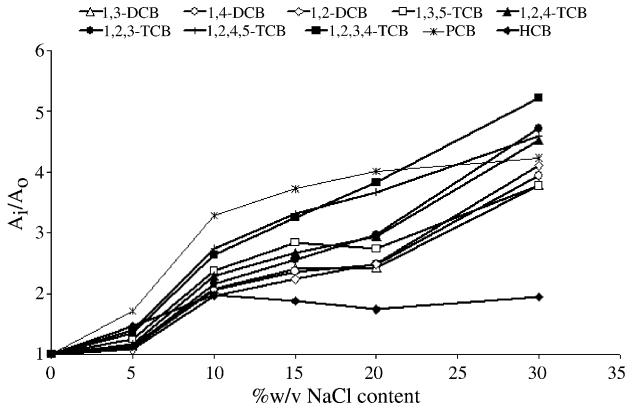

Fig. 2. Effect of ionic strength on the extraction efficiency of headspace SDME used for the analysis of chlorobenzenes in water samples. The ratio of peak areas at various salt concentrations to the peak area without salt (A_i/A_0) is given as a function of the ionic strength of the aqueous solution. Other experimental conditions: 50 μg/l concentration level; 10 ml aqueous sample in 15 ml glass vial; 2.5 μl toluene drop volume; 1000 rpm stirring rate; 5 min sampling time.

and accordingly, the amount of target pollutants transferred in the headspace is larger. Furthermore, the headspace volume is decreased, and as such a net increase of the total amount of analytes to be extracted is also expected. Thus, for all subsequent experiments a 10 ml aqueous sample volume (5 ml headspace volume) was used.

As stated previously, stirring the aqueous sample results in a degree of convection of the headspace. Increasing the speed of sample agitation is expected to enhance the rate of extraction of all target analytes, suggesting thus that the aqueous-phase mass transfer corresponds to a limiting step in extraction [16]. In a separate set of experiments the effect of sample agitation on extraction was investigated. For the purpose of these experiments a 2.5 μl toluene drop was used each time to extract for 5 min, at 22 °C (air-conditioned), water samples containing 50 μg/l of all target analytes and stirred at different agitation rates (namely: 0, 400, 700, 1000 and 1250 rpm). As expected, the results revealed that agitation dramatically enhanced extraction reaching a maximum at 1000 rpm. At 1250 rpm (maximum speed of the magnetic stirrer), the stability of the drop was affected and depending on the analyte the resulting analytical signal either decreased or remained the same (when compared to 1000 rpm) [24]. Based on these observations stirring of the sample at 1000 rpm was selected, optimising thus the extraction efficiency for all target analytes.

Headspace SDME is an equilibrium rather than an exhaustive extraction technique [24]. In this context, a series of spiked-water samples were prepared and the variation of the analytical signal for each analyte was studied as a function of exposure time. For the purpose of the present experiments a 2.5 μl of toluene drop was exposed for 1–7 min to the headspace of 10 ml aqueous sample containing 50 μg/l of each target analyte and stirred at 1000 rpm. Longer extraction times were avoided as they typically resulted in significant solvent evaporation. On the basis of the curves obtained (Fig. 1) the only analytes, which appear to reach equilibrium after sampling the headspace for 5 min are PCB and HCB. Nonetheless, for quantitative headspace SDME analysis, it is not necessary for the analytes to have reached equilibrium, only to allow sufficient mass transfer into the organic drop and exact reproducible extraction time [17,23]. To avoid incidents of drop evaporation, due to increased exposure times, a 5 min sampling period was selected for all subsequent analyses.

In order to examine the effect of ionic strength of the sample matrix on extraction (salting-out effect) [23,24,26], a series of experiments were carried out with the aqueous samples containing each time different amounts of NaCl. For the purpose of these experiments, 10 ml aqueous solutions spiked at 50 μg/l with all target analytes and having a salt content ranging from 0 to 30% (w/v) NaCl were extracted using 2.5-μl toluene drops for 5 min. The results are depicted in Fig. 2, where the ratio of peak areas at various salt concentrations (A_i) to the peak area without salt (A_0) is given as a function of the ionic strength of the aqueous solution, demonstrating thus the positive effect of salt on extraction. On the whole, the presence of salt greatly enhanced extraction for all target analytes, reaching a maximum at 30% (w/v) NaCl salt content. Based on these observations, it was decided to maintain the salt content at 30% (w/v) NaCl for all subsequent experiments.

Overall, the optimised extraction conditions found in the present studies were: a 2.5 μl toluene microdrop was exposed for 5 min to the headspace of a 10 ml aqueous sample containing 30% (w/v) NaCl placed in a 15 ml vial and stirred at 1000 rpm. Under these optimum experimental conditions the enrichment factor defined as the ratio between the final analyte concentration in the organic acceptor phase and the initial analyte concentration within the sample was evaluated and was found to range between 157 and 92 for most target analytes except for PCB and HCB that were found to be 31 and 17, respectively.

3.2. Evaluation of headspace SDME performance

The performance of the proposed method was evaluated by extracting for 5 min the headspace of 10 ml aqueous solutions containing 30% NaCl (w/v) stirred at 1000 rpm and spiked with all target analytes using five concentration levels ranging from 0.02 to 50 μg/l. It should be mentioned here, that for all quantification experiments, the organic solvent acceptor phase consisted of a toluene solution of the internal standard. The calculated calibration curves gave a high level of linearity for all target analytes with correlation coefficients (r^2) ranging between 0.9901 and 0.9971, except for HCB where the correlation coefficient was found to be 0.9886 (Table 1). Furthermore, the repeatability of the proposed method, expressed as relative standard deviation (RSD), was evaluated by extracting five consecutive aqueous samples spiked at 1 μg/l with each target analyte and was found to vary between 2.1 and 13.2% with a mean value of 6.7% (Table 1).

The limits of detection (LODs) for all target analytes (Table 1) were determined according to published guidelines at a signal-to-noise ratio (*S*/*N*) of three [27]. They were found to be in the low μg/l level ranging between 0.003 and 0.031 μg/l.

Table 1 also provides the reported LODs values found in the literature for the analysis of chlorobenzenes in water samples when using EPA method 8121 (GC coupled to an electron capture detector—ECD) [28] and those obtained when applying SPE coupled to GC–MS–SIM [8] and headspace SPME coupled to GC–MS–SIM [12]. As can be seen the LODs obtained with headspace SDME are superior to those obtained with EPA method 8121 (except for HCB) as well as with the SPE-based method. Comparison of the present optimised method with headspace SPME shows that the two methods have comparable LODs for most target analytes, with the exception of PCB and HCB. Nonetheless, headspace SDME is a much faster extraction method given that these LOD values were obtained after sampling the water samples for only 5 min instead of 30 min used in the case of headspace SPME. Furthermore, contrary to SPME, the present method requires no dedicated and expensive instrumentation minimising thus the costs of analysis per sample.

During the present investigations, matrix effects upon extraction were also evaluated by investigating the applicability of the proposed method to determine chlorobenzene contamination in natural water samples. Although less applicable when performing headspace analysis of volatile compounds, it is possible that the developed headspace SDME method as an equilibrium technique, may undergo competitive adsorption to suspended solids present in the aqueous matrix, reducing thus the quantity of analyte transferred into the headspace and as a result into the organic acceptor phase. Analyte losses to suspended solids may be more difficult to control [29], and there is always the need to determine their extent. In this context, two separate sets of experiments were performed by extracting in five replicate runs and under the optimised experimental conditions all target analytes from tap and well water samples spiked at 1 μg/l with each chlorobenzene compound. It should be mentioned here, that all samples were initially analysed (under the full-scan and MS–SIM conditions) and were found to be free of all target compounds. For each set of experiments the relative recoveries, determined as the ratio of the concentrations found in environmental and deionised water samples, spiked at the same contamination level, were evaluated [26]. The results summarised in Table 2, show that for the tap water samples relative recoveries ranged between 84 and 99% with a mean value of 94%, and for the well water samples between 82 and 107% with a mean value

Table 1
Main method parameters for the extraction of chlorobenzenes from water samples using the optimized headspace SDME method; Limits of detection (LODs) when using SPME and SPE technique and the ones reported in EPA method 8121

Analyte	Correlation Coefficient (r^2)[a]	RSD (n = 5) (%)[b]	LODs Headspace SDME (μg/l)[c]	LODs EPA 8121 (μg/l)[d]	LODs SPE (μg/l)[e]	LODs Headspace SPME (μg/l)[f]
1,3-DCB	0.9933	2.2	0.003	0.250	0.010	0.006
1,4-DCB	0.9929	2.1	0.006	0.890	NA[g]	0.006
1,2-DCB	0.9931	4.8	0.006	0.270	0.012	0.006
1,3,5-TCB	0.9942	6.7	0.004	0.012	0.019	0.004
1,2,4-TCB	0.9912	6.1	0.006	0.130	0.031	0.004
1,2,3-TCB	0.9938	7.1	0.006	0.039	0.013	0.004
1,2,4,5-TeCB	0.9971	7.5	0.003	0.010	0.020	0.003
1,2,3,4-TeCB	0.9964	4.8	0.003	0.010	0.028	0.003
PCB	0.9901	13.2	0.016	0.038	0.028	0.004
HCB	0.9886	12.9	0.031	0.006	0.045	0.006

[a] Linear range 0.02–50 μg/l (number of calibration points = 5).
[b] Relative standard deviation (RSD); mean value for five replicate analyses; spiking level 1 μg/l.
[c] Limits of detection (LODs) were calculated for a three signal to noise ratio (*S*/*N* = 3).
[d] Data taken from reference [28]; EPA 8121 (GC–ECD).
[e] Data taken from reference [8]; C18 cartridges, 200 ml water samples GC–MS–SIM analysis.
[f] Data taken from reference [12] (PDMS 100 μm SPME fibre, 30 min headspace SPME sampling of 5 ml samples containing 20% (w/v) NaCl, at room temperature stirred at 1500 rpm, GC–MS–SIM analysis).
[g] Not available.

Table 2
Mean relative recoveries and RSD values of the ten chlorobenzene compounds in natural water samples

Analyte	Relative recoveries (%) and RSD values (%) in parentheses[a,b]	
	Tap water	Well water
1,3-DCB	96 (4.3)	102 (6.6)
1,4-DCB	84 (10.1)	98 (7.4)
1,2-DCB	94 (6.1)	104 (7.0)
1,3,5-TCB	92 (11.8)	98 (6.5)
1,2,4-TCB	93 (8.0)	107 (11.0)
1,2,3-TCB	91 (9.5)	100 (4.8)
1,2,4,5-TeCB	96 (10.7)	91 (5.4)
1,2,3,4-TeCB	92 (10.1)	88 (4.4)
PCB	99 (11.7)	87 (10.1)
HCB	98 (19.7)	82 (14.0)

[a] Spiking level: 1 μg/l.
[b] Mean of five replicate analyses.

of 97%. As can be seen, matrix had little effect on the developed headspace SDME method. Relative standard deviation values were ranged between 6.0–20% and 4.0–14%, for tap and well water samples, respectively.

4. Conclusions

A new analytical method comprising headspace SDME coupled with GC–MS has been developed, quantifying trace levels of chlorobenzenes in water samples. Sample preparation time as well as consumption of toxic organic solvents were minimised without affecting the sensitivity of the method. This easy to use and cost-effective method represents an attractive alternative to traditional and recently introduced methods as well as an emerging field of research.

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