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Trace analysis of chlorobenzenes in water samples using headspace solvent microextraction and gas chromatography/electron capture detection

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Abstract

In the present work, a rapid method for the extraction and determination of chlorobenzenes (CBs) such as monochlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene in water samples using the headspace solvent microextraction (HSME) and gas chromatography/electron capture detector (ECD) has been described. A microdrop of the dodecane containing monobromobenzene (internal standard) was used as extracting solvent in this investigation. The analytes were extracted by suspending a 2.5 μl extraction drop directly from the tip of a microsyringe fixed above an extraction vial with a septum in a way that the needle passed through the septum and the needle tip appeared above the surface of the solution. After the extraction was finished, the drop was retracted back into the needle and injected directly into a GC column. Optimization of experimental conditions such as nature of the extracting solvent, microdrop and sample temperatures, stirring rate, microdrop and sample volumes, the ionic strength and extraction time were investigated. The optimized conditions were as follows: dodecane as the extracting solvent, the extraction temperature, 45 °C; the sodium chloride concentration, 2 M; the extraction time, 5.0 min; the stirring rate, 500 rpm; the drop volume, 2.5 μl; the sample volume, 7 ml; the microsyringe needle temperature, 0.0 °C. The limit of detection (LOD) ranged from 0.1 μg/l (for 1,3-dichlorobenzene) to 3.0 μg/l (for 1,4-dichlorobenzene) and linear range of 0.5–3.0 μg/l for 1,2-dichlorobenzene, 1,3-dichlorobenzene and from 5.0 to 20.0 μg/l for monochlorobenzene and from 5.0 to 30 μg/l for 1,4-dichlorobenzene. The relative standard deviations (R.S.D.) for most of CBs at the 5 μg/l level were below 10%. The optimized procedure was successfully applied to the extraction and determination of CBs in different water samples.

Keywords: Headspace solvent microextraction; Chlorobenzenes; Gas chromatography

1. Introduction

Chlorobenzenes (CBs), which can enter the aquatic environment such as solvents, by-product materials of phenol and pesticide manufacturing, chemical contamination, etc., are ubiquitous due to their widespread use during the last several decades [1,2]. CBs are hazardous to health and have been ranked as priority pollutants by the US Environmental Protection Agency (EPA) [3].

Chlorobenzenes are very persistent under the anaerobic conditions usually found in sediment and ground water, but many microorganisms from sediments and sewage sludge have been shown to degrade chlorobenzenes (higher chlorinated compounds are less readily degraded and such degradation occurs only under aerobic conditions) [4].

The following clinical symptoms and signs of excessive exposure in the case of chlorobenzenes have been observed [5]: (a) effects on the central nervous system, (b) irritation of the eyes, (c) irritation of the upper respiratory tract, (d) hardening of the skin, and (e) hematological disorders including anemia.

Recently, headspace solid-phase microextraction (HS-SPME) has been used to extract and determine CBs present in the water samples [3,6–11]. However, despite several advantages of SPME [12], some practical drawbacks for the method have already been reported in the literature [13,14].

Recently, liquid-phase microextraction (LPME) has been developed as a solvent-reduced pretreatment technique which is fast, simple and inexpensive. This novel technique eliminates

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the disadvantages of conventional extraction methods, such as using time-consuming operations and specialized apparatuses. Since very little solvent is used, there is minimal exposure to toxic organic solvent for the operator. At the same time, LPME combines extraction, concentration and sample introduction in one step [15].

LPME technique has been discussed in several papers [16–19]. It is based on the distribution effect of the analytes between a microdrop of organic solvent at the tip of a microsyringe needle and the aqueous solution. The organic solvent drop is first exposed to the sample solution and target analytes are extracted from the sample matrix into the drop. After the equilibrium is reached, the drop with concentrated analytes is then transferred to the injection port of a gas chromatography for analysis.

Headspace solvent microextraction (HSME) is very similar to LPME except that a microdrop of high boiling extracting solvent is exposed to the headspace of a sample. The drop is then withdrawn into the syringe and injected into the GC. The microdrop essentially performs the same function as the fiber in SPME: the extraction and concentration of headspace components into a small volume of solvent which can then be injected into the GC [20]. Although the headspace extraction mode was first reported in 2000 [21], recently Theis et al. [22] has described detailed kinetic studies of the headspace mode.

The main objective of this paper is to study the applicability of HSME followed by GC with ECD to determine CBs in water samples. Experimental parameters affecting the extraction of the studied CBs, such as the nature of the extracting solvent, microdrop and sample temperatures, the stirring rate, microdrop and sample volumes, the ionic strength and extraction time, were optimized. Under the optimized experimental conditions, the detection limit and the dynamic linear range of the proposed method were then evaluated.

2. Experimental

2.1. Reagents and materials

Dodecane (99.5%, Merck) was used as received for the preparation of all standard solutions. Methanol (99.9%) and sodium chloride (99.5%) were obtained from Merck. *Iso*-octane (99.0%) and toluene (99.8%) were obtained from Fluka. Monochlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene and monobromobenzene with the highest purity available were obtained from Merck. Double distilled water was used for preparing working standard solutions. Nitrogen (99.999%) was obtained from Roham Gas Company (Tehran, Iran).

The stock standard solutions of chlorobenzenes (1000 mg/l) were prepared in MeOH and were stored and refrigerated at 4 °C. These stock standard solutions were diluted with methanol to prepare a mixed stock of analytes in such a way that the concentration of mixture was 0.5 mg/l with respect to monochlorobenzene, 1,2-dichlorobenzene and 1,3-dichlorobenzene and 5 mg/l respect to 1,4-dichlorobenzene. Then, working standard solutions were freshly prepared by diluting the mixed standard solution with doubly distilled water to the required concentrations.

A solution of 100 mg/l of bromobenzene (internal standard) was prepared in dodecane. This solution was used as extracting solvent.

2.2. Instrumentation

The extraction and injection procedures were carried out using a 10-μl SGE microsyringe (Code: 5B-7). A magnetic stirrer (Heidolph MR 3001K) and an 8 mm × 1.5 mm stirring bar were used to stir the solution. Two separate recirculation cell compartments connected to two corresponding water baths were employed to control the temperature of the syringe needle and the sample solution, respectively. A two compartment-recirculating cell made of glass was used for controlling the sample solution temperature. A second cell fabricated with similar substance in outside and an inner tube made of stainless steel (with a 1/16-in. outer diameter) was employed to control the needle temperature. In order to reach a temperature very close to that of the cooling bath, the internal surface of the inner tube was just touching the external surface of the microsyringe needle.

The GC–ECD analysis was performed using a Varian CP-3800 gas chromatograph equipped with an electron capture detector and a DB-5 (5% biphenyl + 95% poly dimethyl siloxane) fused-silica capillary column (25 m × 0.32 mm i.d. and 1.2 μm film thickness). The injector and detector temperatures were 270 and 280 °C, respectively. The injection port was operated at a 1:30 split to allow for greater sensitivity. A constant flow (2 ml/min) of nitrogen was used as a carrier gas. The analysis was performed with an initial column temperature of 80 °C held for 2 min followed by heating to 100 °C at 10 °C/min, followed by heating to 110 °C at 1 °C/min, and finally, followed by heating to 250 °C at 60 °C/min and holding at 250 °C for 10 min to clean the column.

2.3. Analytical procedure

A 7 ml aliquot of the sample solution was placed in the 10 ml vial with a PTFE-silicon septum (Supelco). The SGE syringe was completely washed with methanol, and then with acetone. After drying the syringe, it was rinsed and primed for at least seven times with the solvent/internal standard solution. After the uptake of 2.5 μl of the extracting solvent, the needle of the syringe was then inserted into the internal tube of the two compartment cells above the extraction vial and having pierced the vial septum, it was then clamped. By applying the two compartment cells, the needle tip was located in a constant position in the headspace of solution. To begin the extraction process, the syringe plunger was depressed and a microdrop of extraction solvent was suspended from the needle tip. After extracting for a prescribed time, the plunger was withdrawn and the microdrop was retracted back into the syringe. The needle was then removed from the vial and its contents were injected into the GC for the analysis. Finally, the analytical signal was shown as the relative peak area of the analyte to

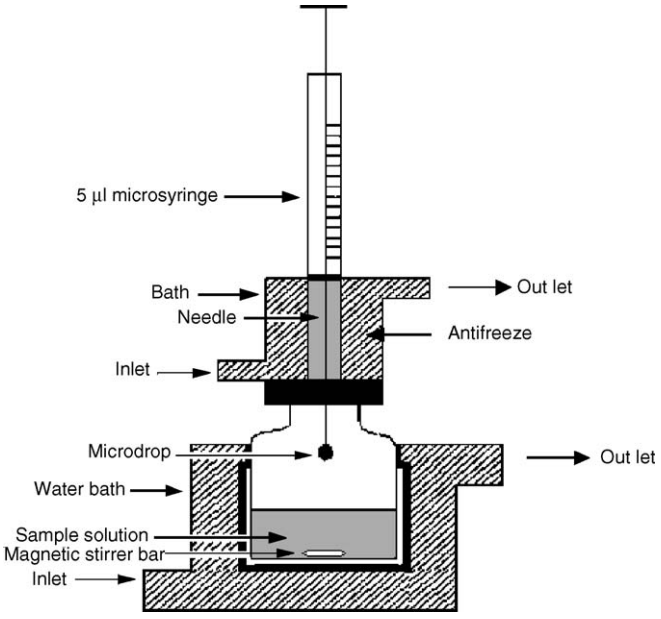

Fig. 1. Schematic diagram of the headspace solvent microextraction apparatus.

the internal standard. Fig. 1 shows the apparatus used for the HSME.

3. Results and discussion

This study explored the applicability of HSME to the analysis of CBs in aqueous matrices. The effect of a number of variables, including the type of solvent, microdrop and sample temperatures, the stirring rate, microdrop and sample volumes, the ionic strength and extraction time, on the sensitivity of the method was examined.

The HSME theory indicates that analytes in headspace are transferred into the organic solvent extruded from the needle tip of a microsyringe; a dynamic equilibrium is finally established between the concentration of the analytes in headspace and that of analytes in the organic solvent drop. The amount of the analyte, n, extracted by the microdrop at equilibrium is described by the following equation [23]:

$$n = \frac{k_{odw} V_d C_0 V_s}{k_{odw} V_d + k_{hs} V_h + V_s} \quad (1)$$

where k_{odw} and k_{hs} are the organic drop-water (sample) and the headspace-water distribution constants, respectively; C_0 the initial concentration of the analyte in the matrix; and V_d, V_s and V_h are the volumes of the drop, the sample, and the headspace, respectively. In Eq. (1) relationships between n and other parameters such as k_{odw}, V_d, V_s and V_h are clear. These parameters are very important for optimizing the extraction conditions.

3.1. Selection of extracting solvent

Careful attention should be paid to the selection of the extraction solvent. First, it should have a high boiling point and low vapor pressure in order to reduce the risk of evaporation. Second, the solvent should have good chromatographic behavior. Third, the partitioning coefficient should be high. Finally, high-purity organic solvents are necessary [24]. According to these considerations, three solvents, toluene, *iso*-octane, and dodecane were considered. Among different extracting solvents tested, the use of dodecane resulted in the best extraction efficiency, while its chromatographic peak was easily separated from the sample peaks. Thus, dodecane was chosen as the extracting solvent in this investigation. In order to improve the precision and accuracy of the method, monobromobenzene was used as an internal standard.

3.2. Addition of salt

The salting-out effect has been used universally in SPME and LLE. The addition of salt to an analytical sample can potentially increase the analyte recovery in the microextraction procedures [12]. NaCl at a concentration range of 0–4 M was therefore added to water samples to evaluate its effect on the extraction efficiency. The extraction efficiency improved with an increasing salt concentration to a maximum value of 2 M. The same phenomenon has been previously reported [25].

It is evident that the addition of NaCl promotes the transport of the analytes to the headspace and hence to the extraction drop. This can be explained by the fact that water molecules form hydration spheres around the salt ions. These hydration spheres reduce the concentration of water available to dissolve analyte molecules; hence, it is expected that this will drive additional analytes into the extraction phase [26].

3.3. Sample temperature

We expected that an increase in the sampling temperature would in turn increase the absorption of the analytes on a dodecane drop because of the increase in analyte concentration in the headspace. The effect of sampling temperature was studied by exposing an extracting drop 5 min in the headspace at 25–55 °C. The extraction curves showed that the amount of the analytes absorbed increases by increasing the temperature up to 45 °C. This can be explained by the fact that at higher temperatures the vapor pressure of the analytes and hence their concentrations in the headspace will increase. At higher temperatures, the amount of the analytes extracted decreases, probably due to the decrease of K_{odw}. Hence, the optimum sampling temperature for a fixed extraction time of 5 min was 45 °C.

3.4. Sample volume

The effect of the sample volume on the extraction efficiency was investigated. As indicated by Eq. (1), an increase in sample volume and consequently a decrease in headspace volume enhance the extracted amount of analyte, which improves the sensitivity.

The experiments were performed using 10 ml vials and the volume of the sample was increased from 1 to 9 ml. The relative peak areas obtained for each analyte with different sample volume are shown in Fig. 2. A nearly linear increase in response was observed for these compounds upon increasing the sample

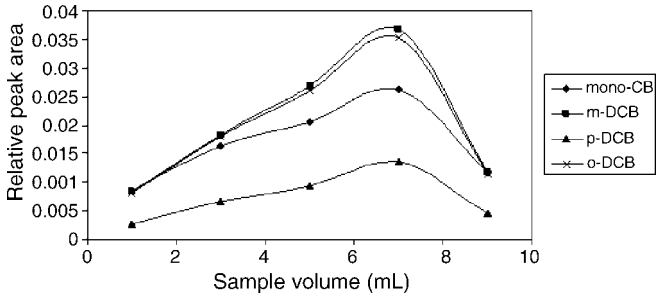

Fig. 2. Influence of sample volume on the relative peak area of CBs. Extraction conditions: drop volume, 2.5 μl; extraction time, 5 min; microsyringe needle temperature, 6 °C; stirring rate, 300 rpm; NaCl concentration, 2 M, sample temperature, 45 °C.

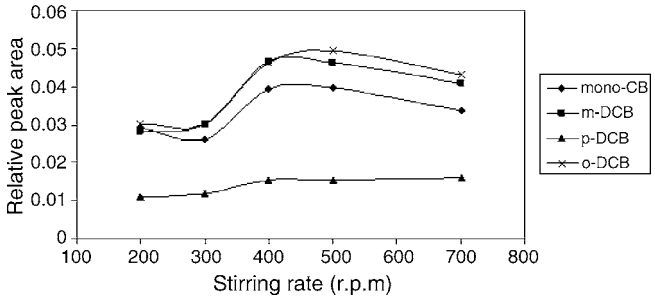

Fig. 3. Influence of stirring rate on the relative peak area of CBs. Extraction conditions: drop volume, 2.5 μl; extraction time, 5 min; sample volume, 7 ml; sample temperature, 45 °C; NaCl concentration, 2 M; microsyringe needle temperature, 6 °C.

volume up to 7 ml. At higher volumes, a sharp decrease in signal was observed. This observation can be explained by the fact that in these experiments, the stirring speed is only 300 rpm. Thus, when stirring the solution with large volume at a fixed rate, the convection is not as well as in the aqueous phase with small volume, resulting in less efficient extraction.

3.5. Microsyringe needle temperature

If exhaustive extraction is not achieved by HSME, the amount of analytes absorbed in the drop will also depend upon the temperature. The amount of analytes absorbed in the drop increases by decreasing the microdrop temperature because the process of analyte absorption in the microdrop is exothermic. If a low microdrop temperature is maintained during sampling, the sensitivity should increase significantly.

The temperature of the microsyringe needle was changed in the range of 0–9 °C and its effect on the extraction efficiencies of CBs compounds was investigated. It was shown that by increasing the microsyringe needle temperature, the extraction efficiencies of all CBs tend to decrease. Thus, the microsyringe needle temperature was adjusted at 0 °C for further studies.

3.6. The stirring rate

Stirring rates can increase the extraction efficiency by means of reducing the Nernst diffusion layer and increasing the extraction rate.

Based on the penetration theory of mass transfer of solute, the aqueous phase mass-transfer coefficient of solute β_{aq} is given by

$$\beta_{aq} = 2\sqrt{\frac{D_{aq}}{\pi t_c}} \quad (2)$$

where D_{aq} is the diffusion coefficient in the aqueous phase, and t_c is the exposure time of a small fluid volume element of one phase momentarily in contact with the other phase [18]. According to the theory, β_{aq} increases with increasing the stirring rate because at a faster stirring rate, the value of t_c is smaller [18]. As a result, the agitation enhanced the extraction efficiency.

As shown in Fig. 3, the peak areas of all analytes increase by increasing the stirring rate up to 500 rpm. Higher stirring rates (>700 rpm) were not used because of spattering, which damaged the drop. Hence, in further studies, a stirring rate of 500 rpm was chosen.

3.7. The extraction time

For enhancing the repeatability of the analysis, it is necessary to choose a time at which equilibrium is reached between the extracting phase, the headspace and the water sample. The equilibrium was examined by exposing the solvent drop to the headspace up to 10 min. As shown in Fig. 4, the relative peak area increased quickly with the extraction time until 5 min; after 5 min, no dramatic changes were obtained with additional extraction time. Therefore, in all subsequent optimized experiments, an extraction time of 5 min was used.

3.8. Organic microdrop volume

To increase the sensitivity of the HSME procedure, the organic drop volume was optimized. The theoretical relationship between the amount of analyte extracted and the organic drop volume for the three-phase system is described by Eq. (1). As indicated by Eq. (1), the amount of analyte extracted by the microdrop is related to the volume of the drop, and the sensitivity improves as the volume of the drop increases. Therefore, the experiments were performed by increasing the drop volume from 1.0 to 3.0 μl. As shown in Fig. 5, peak areas of CBs increased with an increase in the drop volume. However, using higher drop

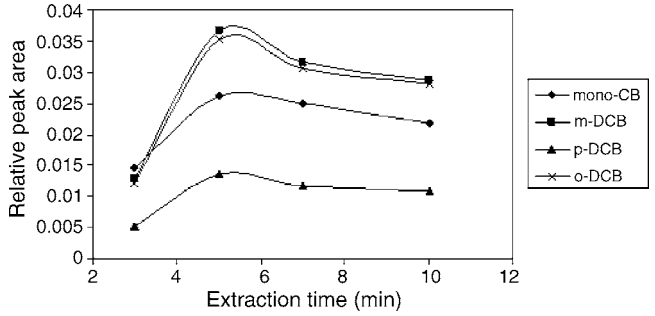

Fig. 4. Influence of extraction time on the relative peak area of CBs. Extraction conditions: microsyringe needle temperature, 0 °C; sample volume, 7 ml; stirring rate, 500 rpm; sample temperature, 45 °C; NaCl concentration, 2 M, drop volume, 2.5 μl.

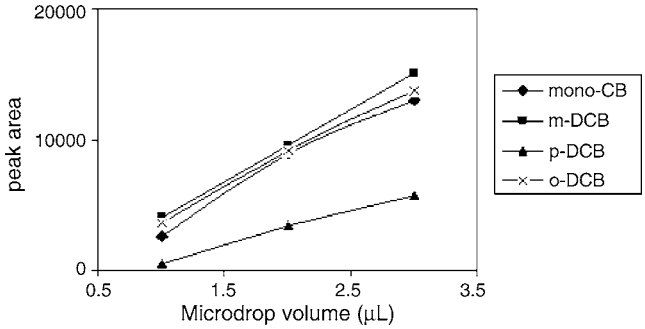

Fig. 5. Influence of microdrop volume on the relative peak area of CBs. Extraction conditions: microsyringe needle temperature, 0 °C; sample volume, 7 ml; stirring rate, 500 rpm; sample temperature, 45 °C; NaCl concentration, 2 M, extraction time, 5 min.

volumes of organic solvent can result in the loss of the organic drop. To avoid this loss, drop volumes of 2.5 μl were considered in further experiments.

3.9. Evaluation of the method of performance

Calibration curves were drawn using five spiking levels of CBs in the concentration range of 0.5–3.0 μg/l with respect to 1,2-dichlorobenzene and 1,3-dichlorobenzene and 5.0–30.0 with 1,4-dichlorobenzene and 5.0–20.0 μg/l with monochlorobenzene. For each level, three replicate extractions were performed at optimal conditions (extraction temperature, 45 °C; sodium chloride concentration, 2 M; extraction time, 5.0 min; stirring rate, 500 rpm; drop volume, 2.5 μl; sample volume, 7 ml; microsyringe needle temperature, 0.0 °C). The corresponding regression equation, correlation coefficient (r^2), dynamic linear range (DLR) and the limit of detection (LOD) were calculated and summarized in Table 1.

In order to examine the enrichment factor of each analyte, three replicate extractions were performed at optimal conditions from aqueous solutions consisting 5 μg/l monochlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 50 μg/l 1,4-dichlorobenzene. The enrichment factor was calculated as the ratio of the final concentration of the analyte in the microdrop and its concentration in the original solution. The standard solutions of CBs were prepared in dodecane as solvent and the calibration curves were drawn. Finally, the actual concentration of each extracted analyte in dodecane was calculated from the calibration curves and the enrichment factors were determined and summarized in Table 1.

The applicability of this extraction method to the real water samples was investigated for different spiked water samples (tap water, waste water, waste water of sugar factory of Kermanshah and Caspian Sea water). The samples were stored in a refrigerator at 4 °C and analyzed within 72 h of sampling. Tap water was collected from a laboratory. The water samples (except the tap water) were filtered with 0.45 μm cellulose acetate membrane filters (Millipore) to eliminate particulate matters before the analysis. The results for the water samples showed that they were free of CBs contaminations. CBs with 5 μg/l level were spiked into 7 ml water samples to assess matrix effects.

Table 1
Limit of detections, regression equations, correlation coefficients, dynamic linear ranges, R.S.D., and enrichment factors for HSME of CBs

Analyte	LOD (μg/l)	r^2	Regression equation	DLR (μg/l)	Enrichment factor
Monochlorobenzene	1.9	0.9936	$y = 0.0591C$ (μg/l) + 0.3211	5.0–20.0	1347.4
1,3-Dichlorobenzene	0.1	0.9993	$y = 0.0537C$ (μg/l) + 0.2181	0.5–3.0	1291.8
1,4-Dichlorobenzene	3.0	0.9943	$y = 0.0120C$ (μg/l) + 0.1415	5.0–30.0	40.1
1,2-Dichlorobenzene	0.2	0.9977	$y = 0.0425C$ (μg/l) + 0.1544	0.5–3.0	774.1

Table 2
Determination of CBs in spiked water samples

Sample	Compound	Add (μg/l)	Found (μg/l)	%Recovery	%R.S.D.
Tap water	Monochlorobenzene	5.0	5.3	106.2	10.8
	1,3-Dichlorobenzene	5.0	5.3	105.7	3.4
	1,4-Dichlorobenzene	50.0	51.2	102.5	2.5
	1,2-Dichlorobenzene	5.0	5.2	104.1	8.8
Waste water	Monochlorobenzene	5.0	5.3	106.0	11.3
	1,3-Dichlorobenzene	5.0	5.3	105.7	5.3
	1,4-Dichlorobenzene	50.0	50.9	101.9	4.8
	1,2-Dichlorobenzene	5.0	5.2	104.1	6.7
Waste water of sugar factory of Kermanshah	Monochlorobenzene	5.0	5.3	105.5	12.0
	1,3-Dichlorobenzene	5.0	5.3	105.7	6.1
	1,4-Dichlorobenzene	50.0	50.9	101.9	6.3
	1,2-Dichlorobenzene	5.0	5.2	104.1	6.8
Caspian Sea water	Monochlorobenzene	5.0	5.3	105.6	12.6
	1,3-Dichlorobenzene	5.0	5.1	102.2	8.5
	1,4-Dichlorobenzene	50.0	50.7	101.5	9.1
	1,2-Dichlorobenzene	5.0	5.1	102.1	7.9

Table 3
Determination of trichlorobenzenes in spiked water samples

Sample	Compound	Add (μg/l)	Found (μg/l)	%Recovery	%R.S.D.
Distilled water	1,2,3-Trichlorobenzene	5.0	4.9_8	99.6	6.3
	1,2,4-Trichlorobenzene	5.0	4.9_4	98.8	5.5
Tap water	1,2,3-Trichlorobenzene	5.0	5.2_4	104.8	8.5
	1,2,4-Trichlorobenzene	5.0	5.3	106	9.1

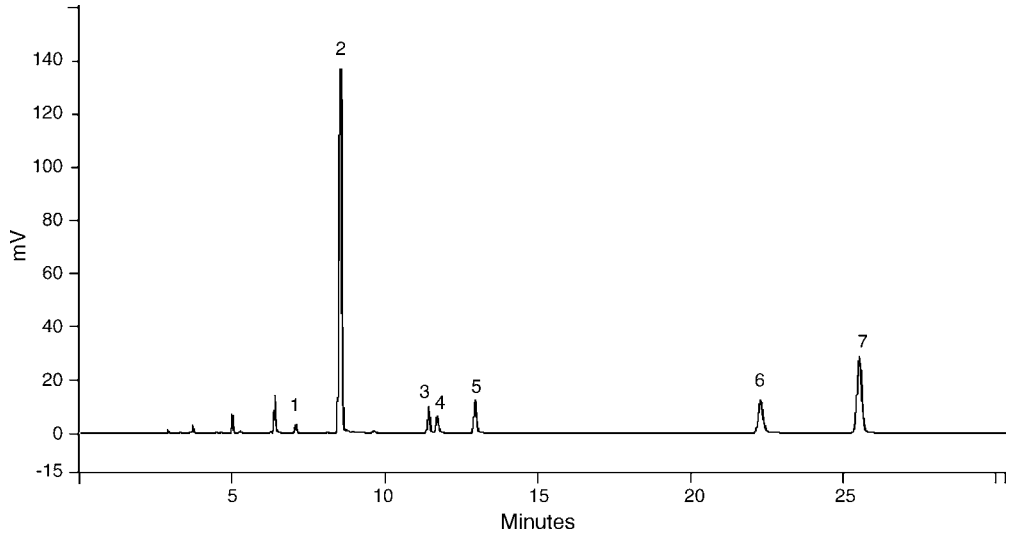

Fig. 6. ECD chromatogram of a 5 μg/l all CBs except 1,4-dichlorobenzene (50 μg/l) spiked tap water sample solution after HSME at optimum conditions. Column temperature programming: 80 °C for 2 min, then increased to 100 °C at 20 °C/min and held for 1 min, followed by a second ramp (1 °C/min) to 125 °C and held for 2 min, and followed by a third ramp (50 °C/min) to a final temperature of 260 °C. (1) Monochlorobenzene; (2) monobromobenzene; (3) 1,3-dichlorobenzene (4) 1,4-dichlorobenzene; (5) 1,2-dichlorobenzene; (6) 1,2,3-trichlorobenzene; (7) 1,2,4-trichlorobenzene.

For the same spiked amount, the calibration curves from distilled water have different slopes than those obtained for other spiked waters, meaning that a significant matrix effect occurs, influencing the partitioning process and recovery. Thus, the determination of CBs was performed using the standard addition method. The percentage of the recoveries of CBs from different water samples ranged from 101.5 to 106.2 (Table 2).

To examine the applicability of the proposed method to additional chlorobenzenes, extraction and determination of 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene in two spiked water samples at optimum conditions were performed (Table 3). As seen, quantitative extraction and determination of trichlorobenzenes (as well as mono and dichlorobenzenes) in water samples at 5 μg/l concentration with R.S.D.s in the range of 5.5–9.1 is possible.

A chromatogram of tap water sample spiked with different chlorobenzenes after the HSME with a 2.5 μl drop of dodecane containing 100 mg/l monobromobenzene as internal standard is shown in Fig. 6.

4. Conclusions

The quantification of CBs by HSME illustrates its use as an alternative methodology that is almost solvent-less as compared with the classical liquid–liquid extractions and significantly less expensive by drawing a comparison between the cost of a droplet and the cost of a fiber with the SPME technique.

The developed technique, HSME, has a number of advantages, including: (1) renewable drop (no sample carryover); (2) high sensitivity and low detection limit; (3) good precision; (4) wide selection of available solvents; (5) low cost; (6) simplicity and ease of use; (7) minimal solvent use; (8) short preconcentration time; (9) possibility of automation; (10) requiring no conditioning (as is the case with the fiber in the solid-phase microextraction); (11) no need for instrument modification.

In comparison with the purge and trap, the proposed method is advantageous in terms of its simplicity and low cost, while it has a limit of detection in the same range as that of purge and trap. Since a fresh organic solvent is used for each extraction, there is no memory effect. Making a comparison between this technique with that of solid-phase microextraction for the determination of CBs in water samples reveals that the precision of HSME is better than that presented in Ref. [25] and at least similar to that of the HS-SPME method [3]. Also, the HSME appears to offer two distinct advantages over the HS-SPME. First, the choice of solvents is virtually unlimited, as compared to the number of the phases currently available for the SPME method. Second, the cost of microliters of the solvent required for the HSME is negligible as compared to the cost of the commercially prepared SPME fibers. It should be noted that the apparatus involves a magnetic stirring, a glass vial, two

circulating water baths and a microsyringe, among which the water baths are the main costly parts. Moreover, in each extraction, only 2.5 μl of dodecane of a very low cost is necessary. In addition, the absence of the solvent peak in the HS-SPME chromatogram is an obvious advantage. By using splitless injection and mass spectrometry, LODs 25–500 times lower than that of HSME for chlorobenzenes were obtained [3]. It is noteworthy that by employing mass spectrometry instead of ECD, improved LODs likely could be attained in the proposed method.

References

[1] J.E.M. Beurskens, C.G.C. Dekker, H. Van den Heuvl, M. Swart, J. de Wolf, J. Dolfing, Environ. Sci. Technol. 28 (1994) 701.
[2] B. Karnofsky, Hazardous Waste Management Compliance Handbook, 2nd ed., Van Nostrand Reinhold, New York, 1997.
[3] Y. He, Y. Wang, H.K. Lee, J. Chromatogr. A 874 (2000) 149.
[4] L. Wolska, P. Konieczka, A. Jastrzebska, J. Namiesnik, J. Chromatogr. Sci. 41 (2003) 53.
[5] B.G. Oliver, K.D. Bothen, Int. J. Environ. Anal. Chem. 12 (1982) 131.
[6] M. Giardina, L.H. Ding, S.V. Olesik, J. Chromatogr. A 1060 (2004) 215.
[7] H.A. Leslie, J.L.M. Hermens, M.H.S. Kraak, Environ. Toxicol. Chem. 23 (2004) 2017.
[8] A. Paschke, P. Popp, J. Chromatogr. A 1025 (2004) 11.
[9] D.H. Wang, J. Xing, J.G. Peng, C.Y. Wu, J. Chromatogr. A 1005 (2003) 1.
[10] Z. Takats, K. Torkos, Chromatographia 48 (1998) 74.
[11] J. Liu, K. Hara, S. Kashimura, T. Hamanaka, S. Tomojiri, K. Tanaka, J. Chromatogr. B 731 (1999) 217.
[12] J. Pawliszyn, Solid Phase Microextraction: Theory and Practice, Wiley, New York, 1997.
[13] H. Prosen, L. Zupancic-Kralj, Trends Anal. Chem. 18 (1999) 272.
[14] M.F. Apendurda, J. Chromatogr. A 889 (2000) 3.
[15] R. Zhao, W. Lao, X. Xu, Talanta 62 (2004) 751.
[16] S. Shariati-Feizabadi, Y. Yamini, N. Bahramifar, Anal. Chim. Acta 489 (2003) 21.
[17] Y. He, H.K. Lee, Anal. Chem. 69 (1997) 4634.
[18] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 69 (1997) 235.
[19] E. Psillakis, N. Kalogerakis, J. Chromatogr. A 938 (2001) 113.
[20] J.M. Kokosa, A. Przyjazny, J. Chromatogr. A 983 (2003) 205.
[21] A. Przyjazny, J.F. Austin, A.T. Essenmacher, Proceedings of the Sixth Polish Conference on Analytical Chemistry, vol. 2, Gliwice, Poland, 9–14 July, 2000, pp. 135–136.
[22] A.L. Theis, A.J. Waldack, S.M. Hancen, M.A. Jeannat, Anal. Chem. 73 (2001) 5651.
[23] A. Przyjazny, J.M. Kokosa, J. Chromatogr. A 977 (2002) 143.
[24] G. Shen, H.K. Lee, Anal. Chem. 75 (2003) 98.
[25] Y.P. Liu, W.H. Ho, J. Chin. Chem. Soc. 47 (2000) 415.
[26] H. Lord, J. Pawliszyn, J. Chromatogr. A 902 (2000) 17.