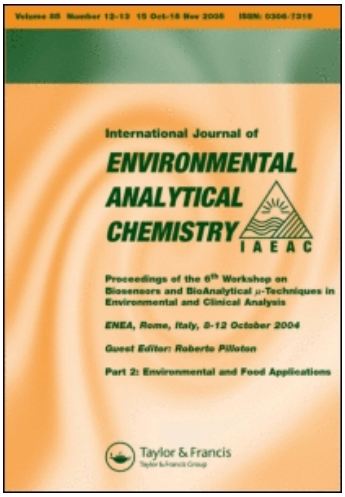

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Dispersive liquid–liquid microextraction (DLLME) coupled with gas chromatography–electron capture detection (GC–ECD), has been developed for the extraction and determination of 14 organochlorine pesticides (hexachlorocyclohexanes (α-HCH, β-HCH and δ-HCH), Lindane (γ-HCH), Aldrin, Dieldrin, Endrin, Heptachlor, Heptachlor epoxide, α-Chlordane, β-Chlordane and p,p′-DDT, p,p′-DDD, p,p′-DDE) in river water samples. Factors relevant to the microextraction efficiency, such as the kind of extraction and disperser solvent, their volume and the salt effect was investigated and optimised. In this method the appropriate mixture of extraction solvent (13.5 μL carbon disulphide) and disperser solvent (0.50 mL acetone) were rapidly injected into the aqueous sample by syringe. The values of the detection limit of the method were in the range of 0.05–0.001 μg L^{-1}, while the relative standard deviations for five replicates varied from 2.7 to 9.3%. A good linearity ($0.9894 \leq r^2 \leq 0.9998$) and a broad linear range (0.01–200 μg L^{-1}) were obtained. The method exhibited enrichment factors ranging from 647 to 923, at room temperature. The relative standard deviations varied from 2.7 to 9.3% ($n = 5$). The relative recoveries of each pesticide from water samples at spiking levels of 2.00 and 10.0 μg L^{-1} were 88.0–111.0% and 95.8–104.1%, respectively. Finally, the proposed method was successfully utilised for the preconcentration and determination of the organochlorine pesticides in the Jajrood River water samples.

Keywords: dispersive liquid–liquid microextraction; organochlorine pesticides; gas chromatography; river water

1. Introduction

Organochlorine pesticides (OCPs) are a group of chemicals which are used in agriculture to protect trees and crops from pest attack [1]. As a result of their widespread use, OCPs were found to contaminate crops and natural water, for example wells and rivers. These chemicals are known to disrupt the hormone endocrine system and induce cancer in different organisms, thereby posing a significant risk to natural ecosystems and human health [2]. Traditionally, determination of trace levels of OCP residues in aqueous samples relies on the liquid–liquid extraction (LLE) [3–5] and solid-phase extraction (SPE) [6–8]. The most popular technique used is LLE, which requires large quantities of expensive and

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toxic solvents that can pollute the environment. The procedure itself is time-consuming, tedious and often requires preconcentration of the sample prior to analysis. SPE overcomes some of the disadvantages encountered with LLE, as it is less time-consuming and requires little solvent. Solid-phase microextraction (SPME) [9–12], liquid-phase microextraction (LPME) using single drop solvent [13–15], headspace solid-phase microextraction (HS-SPME) [16–18] and stir bar sorptive extraction (SBSE) [19,20] are more recent extraction procedures that have been developed for extraction of OCPs from aqueous samples. For rapid monitoring of OCPs in drinking water risk assessment, sensitive, rapid, and simple analytical methods are therefore necessary.

Recently a new extraction technique called dispersive liquid–liquid microextraction (DLLME) has been reported [21,22]. In this method, an appropriate mixture of extraction and disperser solvent is rapidly injected using a syringe, into an aqueous sample, after which a cloudy solution is formed. Numerous papers on DLLME have been published recently for determining various groups of organic compounds as organophosphorous pesticides, chlorophenols, polycyclic aromatic hydrocarbons, trihalomethanes, bisphenol A and amide herbicides in water samples [21–25], wines [26] and some fruits [27]. The combination of this technique with other analytical instruments like HPLC [28], atomic absorption spectroscopy [29,30], has already been performed. GC techniques are widely used in comparison with other methods, which is due to the easy availability of more highly developed detectors and hyphenated techniques based on GC separations. High enrichment factor, simplicity of operation, rapidity and low cost are advantages of this method.

The aim of this study is to evaluate the effectiveness of DLLME procedure for extraction and determination of 14 OCPs in water samples, collected from two parts of the Jajrood River.

2. Experimental

2.1 *Chemicals and reagents*

All OCPs included in this study; Hexachlorocyclohexanes (α-HCH, β-HCH and δ-HCH), Lindane (γ-HCH), Aldrin, Dieldrin, Endrin, Heptachlor, Heptachlor epoxide, α-Chlordane, β-Chlordane and p,p′-DDT, p,p′-DDD, p,p′-DDE were purchased from Supelco (Bellefonte, PA, USA). Tetrachloroethylene, carbon disulphide, carbon tetrachloride, acetone, acetonitrile, methanol (suprasolv for GC), sodium chloride and phenanthrene (as internal standard) were obtained from E. Merck (Darmstadt, Germany). Each OCP was prepared in methanol at a concentration of $10\,mg\,L^{-1}$ per pesticide. A working standard solution of $1.00\,\mu g\,mL^{-1}$ per pesticide was prepared by stock dilution in methanol. The standard solutions were stored at 4°C. Doubly-distilled water was used for preparation of aqueous solutions.

River water samples were collected from upstream and downstream of Jajrood River from the area of north of Tehran in April 2007 and stored in the dark at 4°C. Prior to analysis, river water samples were filtered through a 0.45 μm membrane filter (MSI, Westboro, MA, USA).

2.2 *Instrumentation and condition*

A Shimadzu 17A GC system (Tokyo, Japan) equipped with an electron capture detector (^{63}Ni) was employed for the analysis of OCPs. The capillary column for GC determination

was a fused-silica BPX5 column (25 m × 0.25 mm i.d., film thickness 0.25 μm, SGE, Australia). The working parameters were: injector temperature, 250°C; carrier gas He (99.9999%), 35 cm/s; oven condition, initial temperature 50°C, held for 2 min, then increased by 10°C min^{-1} to 300°C and held for 3 min. Ultra pure nitrogen (99.9999%), as makeup gas for ECD at the flow of 35 mL min^{-1}; injection mode, splitless; injection volume 2.00 μL. The Hettich Scientific centrifuge (model Hittich, Universal, USA) was used to centrifuge.

2.3 *Extraction procedure*

Five mL aliquot of water sample (doubly-distilled water or river water) was placed in a 10 mL screw cap glass test tube with conical bottom and spiked at level of 1.00 μg L^{-1} of OCPs and phenanthrene (as internal standard). 0.5 mL of acetone (as disperser solvent) plus 13.5 μL carbon disulphide (as extraction solvent) was rapidly injected into each sample solution by a 1.00 mL Hamilton syringe (Reno, NV, USA) and the mixture was gently shaken. A cloudy solution (water/acetone/carbon disulphide) was formed in the test tube. In this step, the OCPs in water sample were extracted into the fine droplets of carbon disulphide. Then, the mixture was centrifuged for 3 min at 3500 rpm. The dispersed fine fragment of extraction solvent was separated at the bottom of conical tube. Then 2.00 μL of settled phase was removed using 1.00 μL zero dead volume, Hamilton syringe (Bonaduz, Switzerland) and injected into the GC. The total volume of the settled phase was determined using a 10.0 μL micro syringe which was about 5.0 ± 0.2 μL.

2.4 *Quantitative evaluation*

In order to evaluate the effect of different experimental parameters such as the type and volume of the extraction and disperser solvents and salt addition on the performance of DLLME, the terms of the enrichment factor (EF) and the extraction recovery (R) were calculated from Equations (1) and (2), respectively.

$$EF = C_{sed}/C_0 \quad (1)$$

where C_{sed} and C_0 are concentration of analyte in settled phase and initial concentration of analyte in aqueous sample, respectively.

$$R\% = (V_{sed}/V_{aq})EF \times 100 \quad (2)$$

where V_{sed} and V_{aq} are volumes of settled phase and aqueous sample, respectively.

The detection limits (DL) have been calculated as three times the standard deviation of the blanks divided by the slope of calibration curves [31].

3. Results and discussion

3.1 *Effect of type and volume of the extraction solvent*

The choice of a proper extraction solvent is important for the optimisation of the DLLME process. The solvent should have low volatility and low water solubility in order to be stable during the extraction period, can be separated from the analyte peaks in the chromatogram and it must have higher density than water. Accordingly, several extracting

solvents, including tetrachloroethylene, carbon tetrachloride and carbon disulphide, were examined. In this study, 5.0 μL of settled phase has been chosen as the base volume. A series of sample solutions were studied using 0.50 mL of acetone and different volumes of the extraction solvent to achieve 5.0 μL volume of settled phase. Therefore, 9.5, 11.5 and 13.5 μL of tetrachloroethylene, carbon tetrachloride and carbon disulphide were used, respectively. Three replicate tests were performed for each solvent under the same conditions. In comparison with other solvents, carbon disulphide has been found to show the best recovery percentage (78.9–101.3%) and minimal standard deviation (Table 1).

To optimise the volume of extraction solvent, solutions containing different volumes of carbon disulphide (13.5, 18.5, 23.5 and 28.5 μL) were tested using the same DLLME procedure. Figure 1 shows the curves of settled phase volume and enrichment factor versus volume of extraction solvent. This plot shows that any rise in volume of carbon disulphide leads to significant increase in volume of the settled phase from 5.0 to 20.0 μL and also to a deep decline in the enrichment factor from 769–923 to 254–355. For the volume less than 13.5 μL, the settled phase volume was little so that the collection was difficult. Thus, 13.5 μL of carbon disulphide was selected as optimum volume.

3.2 *Effect of type and volume of the disperser solvent*

Miscibility of disperser solvent in extraction solvent and sample solution is of great importance for the selection of disperser solvent. In order to choose the most proper disperser solvent, acetone, methanol and acetonitrile were examined. The series of sample solutions were tested using 0.50 mL of each disperser solvent plus 13.5 μL of extraction

Table 1. Efficiency of different extraction solvents evaluated for extraction of OCPs by DLLME.

	Recovery (%)		
Compounds	Tetrachloroethylene, mean ± SD	Carbon tetrachloride, mean ± SD	Carbon disulphide, mean ± SD
α-HCH	76.2 ± 3.9	63.6 ± 3.4	94.8 ± 3.1
β-HCH	74.4 ± 3.7	57.2 ± 4.5	88.5 ± 2.9
δ-HCH	73.6 ± 6.1	60.1 ± 4.8	93.4 ± 1.8
Lindane (γ-HCH)	71.1 ± 3.8	62.8 ± 5.1	81.1 ± 4.2
Aldrin	59.3 ± 4.2	43.2 ± 2.8	79.7 ± 2.4
Dieldrin	67.7 ± 5.3	54.3 ± 5.7	81.7 ± 3.3
Endrin	73.0 ± 3.9	49.2 ± 3.8	97.3 ± 2.7
Heptachlor	69.2 ± 5.7	42.7 ± 6.1	78.9 ± 3.6
Heptachlor epoxide	71.8 ± 3.5	39.4 ± 3.8	85.6 ± 2.5
α-Chlordane	64.9 ± 2.6	46.6 ± 4.7	86.7 ± 4.6
β-Chlordane	76.3 ± 4.2	53.9 ± 3.9	89.4 ± 5.1
p,p′-DDT	73.5 ± 3.6	45.6 ± 4.1	82.5 ± 4.3
p,p′-DDD	75.0 ± 4.9	42.4 ± 5.3	101.3 ± 3.8
p,p′-DDE	71.4 ± 3.4	44.1 ± 4.5	91.7 ± 4.8

Extraction conditions: water sample volume, 5.00 mL; dispersive solvent (acetone) volume, 0.50 mL; extraction solvent volume, 9.5 μL tetrachloroethylene, 11.5 μL carbon tetrachloride and 13.5 μL carbon disulphide; settled phase volume, 5.0 ± 0.2 μL; room temperature; concentration of each OCPs 1.00 μg L^{-1} ($n = 3$).

solvent (carbon disulphide). Extraction recovery of acetone, methanol and acetonitrile as disperser solvents were 78.9–101.3, 63.1–103.2 and 68.3–96.5%, respectively (Table 2). Therefore, acetone was chosen because of the best extraction recovery, less toxicity and low cost.

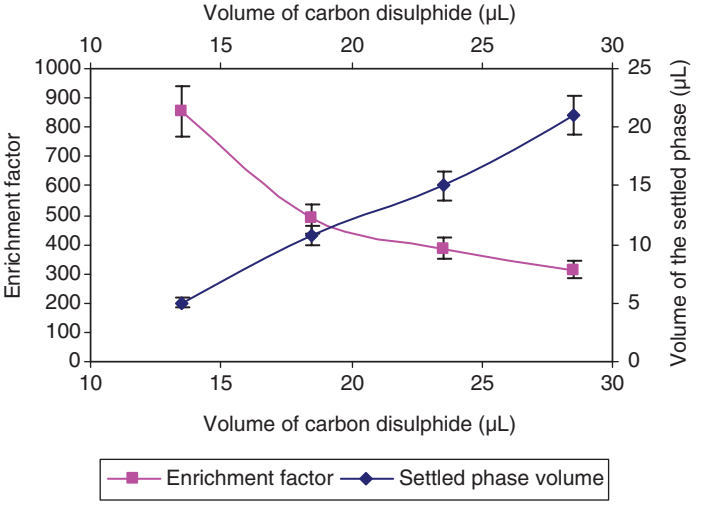

Figure 1. The effect of CS_2 volume on the volume of settled phase and the enrichment factor of the OCPs, obtained from DLLME. Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 0.50 mL at room temperature; concentration of each OCPs, 1.00 μg L^{-1}.

Table 2. Efficiency of different disperser solvents evaluated for extraction of OCPs by DLLME.

	Recovery (%)		
Compounds	Acetone, mean ± SD	Methanol, mean ± SD	Acetonitrile, mean ± SD
α-HCH	94.8 ± 3.1	90.3 ± 4.7	91.3 ± 4.2
β-HCH	88.5 ± 2.9	83.5 ± 5.1	87.9 ± 9.1
δ-HCH	93.4 ± 1.8	91.0 ± 3.9	84.5 ± 6.7
Lindane (γ-HCH)	81.1 ± 4.2	82.5 ± 5.4	75.7 ± 3.9
Aldrin	79.7 ± 2.4	86.1 ± 7.2	73.5 ± 8.2
Dieldrin	81.7 ± 3.3	75.4 ± 6.7	76.3 ± 2.5
Endrin	97.3 ± 2.7	99.8 ± 6.4	95.2 ± 7.4
Heptachlor	78.9 ± 3.6	63.1 ± 7.3	68.3 ± 9.3
Heptachlor epoxide	85.6 ± 2.5	74.5 ± 5.9	77.4 ± 4.9
α-chlordane	86.7 ± 4.6	83.2 ± 6.3	80.9 ± 7.7
β-chlordane	89.4 ± 5.1	81.6 ± 5.7	94.3 ± 4.5
p,p′-DDT	82.5 ± 4.3	86.3 ± 5.9	79.3 ± 4.8
p,p′-DDD	101.3 ± 3.8	103.2 ± 4.8	96.5 ± 6.5
p,p′-DDE	91.7 ± 4.8	79.4 ± 7.9	83.6 ± 5.5

Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone, acetonitrile and methanol) volume, 0.50 mL; extraction solvent (carbon disulphide) volume, 13.5 μL; settled phase volume, 5.0 ± 0.2 μL; room temperature; concentration of each analyte, 1.00 μg L^{-1}($n = 3$).

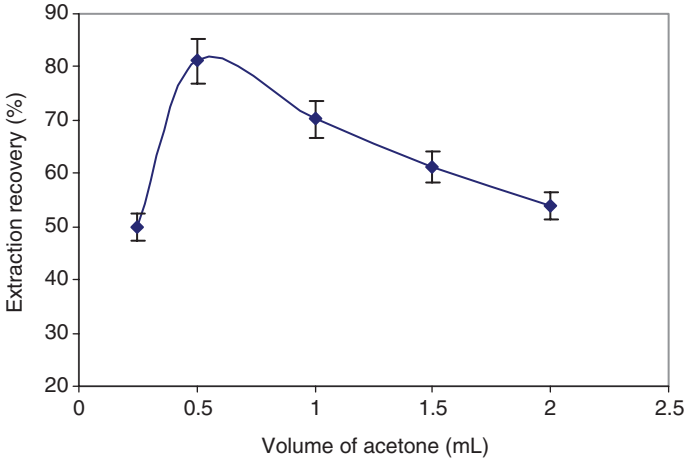

Figure 2. The effect of acetone volume on the extraction recovery of the OCPs, obtained from DLLME. Extraction conditions: water sample volume, 5.00 mL; and settled phase volume, $5.0 \pm 0.2\,\mu L$ at room temperature.

To investigate the effect of volume of disperser solvent on extraction recovery, various volumes of acetone from 0.25 to 2.00 mL plus 13.5 µL of carbon disulphide were used. Figure 2 shows that the extraction efficiency reaches maximum at 0.50 mL acetone volume, after which a steady downward trend is observed. It seems that an increase in the volume of acetone raises solubility of extraction solvent in water sample and falls in the extraction efficiency. On the other part, the cloudy state does not occur at volumes lower than 0.25 mL. Hence, 0.5 mL of acetone was chosen as an optimal volume.

3.3 *The effect of ionic strength*

The influence of salt addition to the extraction efficiency of OCPs utilising DLLME was investigated by addition of various amounts of NaCl (ranging from 0 to 30%, w/v) into the water sample spiked with OCPs at level of $1.00\,\mu g\,L^{-1}$. Other experimental conditions were kept constant. Figure 3 shows extraction recovery and enrichment factor, with respect to the NaCl concentration, and reveals that the addition of NaCl has no significant effect on extraction recovery. The results indicate that an increase in ionic strength causes decrease in solubility of extraction solvent and increase in the volume of settled phase. Therefore, the average of enrichment factors slightly decreases from 904 to 819. Consequently, no salt was added in the further experiments.

3.4 *Method validation*

The coefficient of determinations (r^2), linear ranges (LRs) and the detection limits (DLs) were calculated and recorded in Table 3. DLs, linearity values and coefficient of determinations for the tested OCPs were in the range of 0.05–0.001 $\mu g\,L^{-1}$, 0.01–200 $\mu g\,L^{-1}$ and 0.9894–0.9998, respectively. The repeatability study was carried out by five parallel experiments at the concentration of $1.00\,\mu g\,L^{-1}$ for each of the OCPs under the optimal conditions. The relative standard deviations (RSD) for five replicates varied from 2.7 to 9.3%. Furthermore, the extraction recoveries and enrichment factors ranges were 78.9–101.3% and 647–923, respectively.

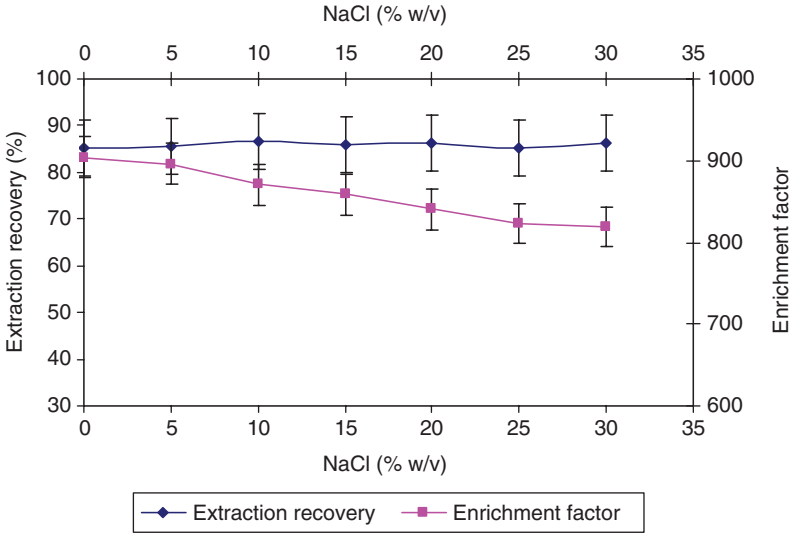

Figure 3. The effect of salt addition on the extraction recovery and enrichment factor of OCPs obtained from DLLME. Extraction solvent (carbon disulphide) volume 13.5 μL; other extraction conditions were as for Figure 1.

Table 3. Quantitative results of DLLME and GC-ECD.

Compounds	DL[a] (μg L^{-1})	r^2	LR[b]	EF[c]	RR[d](%)	RSD[e] (%)
α-HCH	0.004	0.9894	0.01-200	923	94.8	5.6
β-HCH	0.004	0.9981	0.01-200	815	88.5	4.9
δ-HCH	0.004	0.9983	0.01-200	857	93.4	5.2
Lindane (γ-HCH)	0.01	0.9985	0.05-80	769	81.1	6.5
Aldrin	0.009	0.9998	0.07-30	647	79.7	7.1
Dieldrin	0.003	0.9995	0.05-30	726	81.7	5.4
Endrin	0.002	0.9984	0.01-100	803	97.3	2.9
Heptachlor	0.05	0.9991	0.07-30	825	78.9	7.3
Heptachlor epoxide	0.04	0.9989	0.07-30	871	85.6	4.7
α-Chlordane	0.02	0.9990	0.05-80	752	86.7	7.0
β-Chlordane	0.03	0.9992	0.05-80	822	89.4	6.8
p,p′-DDT	0.003	0.9985	0.03-50	779	82.5	3.5
p,p′-DDD	0.006	0.9987	0.03-50	842	101.3	2.7
p,p′-DDE	0.001	0.9989	0.03-50	894	91.7	9.3

[a] Detection limit ($n = 3$).
[b] Linear range ($n = 3$).
[c] Enrichment factor.
[d] Relative recovery.
[e] Relative standard deviation, spiking level 1.00 μg L^{-1} ($n = 5$).

3.5 *Real water analysis*

As an example of the applicability of DLLME, water samples were collected from two parts of the Jajrood River located north of Tehran (Iran) – one from the upstream (A) and another from downstream (B) – and were analysed. To assess the matrix effects, these water samples were spiked with the standards of the target analytes at the concentrations

Table 4. The results obtained from analysis of real water samples.

Compounds	Spiked ($\mu g\,L^{-1}$)	B[†] water sample ($n=3$) Measured ($\mu g\,L^{-1}$) (RSD[a])	RR[b] (%)	A[‡] water sample ($n=3$) Measured ($\mu g\,L^{-1}$) (RSD)	RR (%)
α-HCH	0.00	Nd[c]		Nd	
	2.00	1.90 (10.4)	95.0	2.15 (9.3)	107.5
	10.0	9.73 (7.0)	97.3	10.16 (6.8)	101.6
β-HCH	0.00	Nd		Nd	
	2.00	2.21 (9.8)	110.5	2.07 (8.5)	103.5
	10.0	9.88 (6.6)	98.8	9.96 (5.3)	99.6
δ-HCH	0.00	Nd		Nd	
	2.00	1.97 (2.5)	98.5	1.95 (4.0)	97.5
	10.0	9.93 (6.2)	99.3	9.84 (3.7)	98.4
Lindane (γ-HCH)	0.00	Nd		Nd	
	2.00	1.87 (3.1)	93.5	1.92 (5.9)	96.0
	10.0	9.82 (4.6)	98.2	9.91 (4.7)	99.1
Aldrin	0.00	0.79 (3.3)		Nd	
	2.00	2.89 (7.2)	105.0	2.12 (6.9)	106.0
	10.0	10.82 (5.8)	100.3	10.24 (8.5)	102.4
Dieldrin	0.00	1.37 (4.6)		Nd	
	2.00	3.49 (3.7)	106.0	1.85 (3.2)	92.5
	10.0	11.55 (2.7)	101.8	9.62 (3.9)	96.2
Endrin	0.00	1.12 (5.8)		Nd	
	2.00	2.93 (5.2)	90.5	1.89 (6.2)	94.5
	10.0	10.72 (4.6)	96.0	9.77 (4.9)	97.7
Heptachlor	0.00	Nd		Nd	
	2.00	2.10 (6.6)	105.0	2.12 (7.2)	106.0
	10.0	10.17 (6.2)	101.7	10.13 (5.3)	101.3
Heptachlor epoxide	0.00	Nd		Nd	
	2.00	2.17 (3.7)	108.5	2.07 (4.8)	103.5
	10.0	10.31 (3.4)	103.1	9.96 (2.8)	99.6
α-Chlordane	0.00	Nd		Nd	
	2.00	1.92 (9.5)	96.0	1.76 (7.5)	88.0
	10.0	9.71 (8.1)	97.1	9.58 (6.9)	95.8
β-Chlordane	0.00	Nd		Nd	
	2.00	1.82 (3.4)	91.0	1.92 (4.7)	96.0
	10.0	9.62 (5.1)	96.2	10.04 (3.8)	100.4
p,p′-DDT	0.00	Nd		Nd	
	2.00	2.22 (4.0)	111.0	2.05 (5.9)	102.5
	10.0	10.25 (3.3)	102.5	9.91 (4.2)	99.1
p,p′-DDD	0.00	Nd		Nd	
	2.00	2.21 (4.7)	110.5	2.03 (3.8)	101.5
	10.0	10.41 (2.9)	104.1	9.89 (3.1)	98.9
p,p′-DDE	0.00	Nd		Nd	
	2.00	1.94 (3.5)	97.0	1.98 (4.6)	99.0
	10.0	9.93 (2.7)	99.3	9.95 (3.3)	99.5

Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 0.50 mL; extraction solvent (carbon disulphide) volume, 13.5 μL; settled phase volume, 5.0 ± 0.2 μL; room temperature; [a]Relative standard deviation; [b]Relative recovery; [c]Not detected; [†]B, Downstream; [‡]A, Upstream.

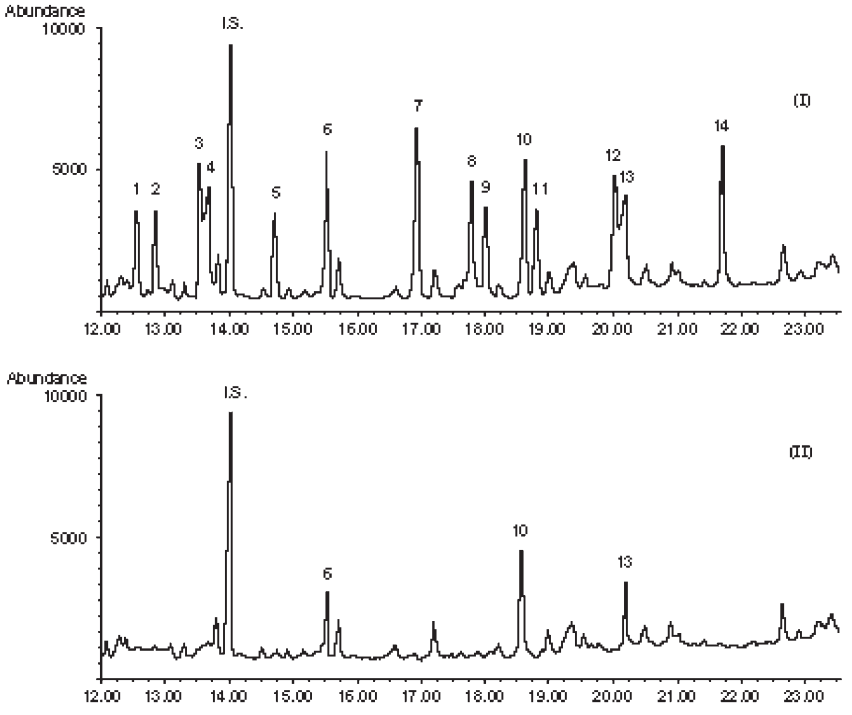

Figure 4. The typical chromatogram of downstream of Jajrood River sample spiked at the concentration level of 2.00 μg L^{-1} for OCPs (I), and sample of downstream (II), obtained using DLLME combined with GC-ECD. Peaks: 1 = α-HCH; 2 = β-HCH; 3 = δ-HCH; 4 = Lindane (γ-HCH); (I.S.) Phenanthrene; 5 = Heptachlor; 6 = Aldrin; 7 = Heptachlor epoxide; 8 = α-Chlordane; 9 = β-Chlordane; 10 = Dieldrin; 11 = p,p′-DDE; 12 = p,p′-DDD; 13 = Endrin; 14 = p,p′-DDT.

of 2.00 and 10.0 μg L^{-1}. For each concentration level, three replicate experiments were made and results are given in Table 4, which indicates that water sample (A) has no OCPs contamination but water sample (B) has Aldrin, Dieldrin and Endrin which are confirmed by spiking OCPs into the water sample (B). The concentrations of Aldrin, Dieldrin and Endrin in water sample (B) were determined to be 0.79 ± 3.3, 1.37 ± 4.6 and 1.12 ± 5.8 μg L^{-1}, respectively. Figure 4 shows the chromatograms obtained from water sample (B) and spiked it at the concentration level of 2.00 μg L^{-1} each OCPs. According to Table 4, relative recoveries for all OCPs in water samples (A and B) were between 88.0–107.5% and 91.0–111.0%, respectively. These results demonstrate that the method is suitable for extraction and determination of OCPs in river water samples.

Comparison of this method with other extraction methods such as SPE [7], SPME [10,18], LPME [15], SBSE [20] and some other techniques [32–34] for extraction and determination of OCPs from water samples signifies that the presented method has some merits. For example, the extraction time in DLLME is very short, less than 5 min, and the extraction equilibrium is achieved very quickly. Extraction times for SPE, LPME, SPME and SBSE range from 10 to 45 min. Precision and linearity of DLLME is comparable with the methods mentioned above. In addition, this method is very simple, rapid, easy to use, inexpensive and environmentally benign. In spite of several advantages of DLLME, portability and on-site applicability appear to be lacking.

4. Conclusion

The developed method is a valuable alternative to classical large-scale methods, since it drastically reduces organic solvent consumption. As can be seen, the limit of detection of DLLME-GC-ECD by only 5.00 mL of sample is comparable to other methods for OCPs. The relative standard deviations (RSDs) of the proposed method are low and the extraction time is very short. The linearity, recovery and enrichment factor of the developed method is suitable. In their entirety, the results revealed that DLLME is a sensitive, rapid and reproducible technique that can be used for the OCPs pre-concentration in river water samples.

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