ANALYTICA CHIMICA ACTA 626 (2008) 166–173

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Development of liquid phase microextraction method based on solidification of floated organic drop for extraction and preconcentration of organochlorine pesticides in water samples

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ARTICLE INFO

Article history:
Received 26 June 2008
Received in revised form
29 July 2008
Accepted 1 August 2008
Published on line 12 August 2008

Keywords:
Liquid-phase microextraction
Organochlorine pesticides
Gas chromatography-electron capture detector
Solidified microdrop

ABSTRACT

A simple and efficient liquid-phase microextraction (LPME) in conjunction with gas chromatography-electron capture detector (GC-ECD) has been developed for extraction and determination of 11 organochlorine pesticides (OCPs) from water samples. In this technique a microdrop of 1-dodecanol containing pentachloronitrobenzene (internal standard) is delivered to the surface of an aqueous sample while being agitated by a stirring bar in the bulk of solution. Following completion of extraction, the sample vial was cooled by putting it into an ice bath for 5 min. Finally 2 μL of the drop was injected into the GC for analysis. Factors relevant to the extraction efficiency were studied and optimized. Under the optimized extraction conditions (extraction solvent: 1-dodecanol; extraction temperature: 65 °C; sodium chloride concentration: 0.25 M; microdrop and sample volumes: 8 μL and 20 mL respectively; the stirring rate: 750 rpm and the extraction time: 30 min), figures of merit of the proposed method were evaluated. The detection limits of the method were in the range of 7–19 ng L^{-1} and the RSD% for analysis of 2 μg L^{-1} of OCPs was below 7.2% ($n = 5$). A good linearity ($r^2 \geq 0.993$) and a relatively broad dynamic linear range (25–2000 ng L^{-1}) were obtained. After 30 min of extraction, preconcentration factors were in the range of 708–1337 for different organochlorine pesticides and the relative errors ranged from −10.1 to 10.9%. Finally the proposed method was successfully utilized for preconcentration and determination of OCPs in different real samples.

1. Introduction

Organochlorine pesticides (OCPs) are a broad class of pesticides that were widely used in the 1950s and 1960s. They can be divided into three groups: benzene hexachloride isomers (e.g. lindane), cyclodienes (aldrin, dieldrin, endrin, chlordane, heptachlor, and endosulfan) and DDT and analogues (methoxychlor, dicofol, and chlorobenzylate) [1]. OCPs have been of great concern due to their persistent nature and chronic adverse effect on wildlife and humans. Despite

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doi:10.1016/j.aca.2008.08.001

the ban and restriction on the usage of OCPs in developed countries during the 1970s and 1980s, some developing countries are still using them for agricultural and public purposes because of the low cost and versatility in controlling various insects [2,3]. Pesticides are mostly moved from agricultural fields to surface water during a surface run-off. The amount lost from fields and transported to surface water depends on several factors, including soil characteristics, topography, weather, agricultural practices, and chemical and environmental properties of individual pesticides [3,4]. Their presence in water is strictly regulated by legislation to concentrations ranging between less than 10 and 100 ng L^{-1} [5–8]. One of the primary goals in water analyses for pesticides is to reach determination limits of about 0.1 μg L^{-1} for individual pesticides and 0.5 μg L^{-1} for total concentrations in order to meet the requirements of the European Union (EU) drinking water directives and those of the US National Pesticide Survey [9,5,10].

Studies involving the determination of OCPs in environmental matrices often deal with samples with low analyte concentrations containing a high number of interferent compounds. Thus, simple and highly sensitive analytical techniques are required to detect and quantify pollutants in water at trace levels [11]. Most determinations of OCPs are based on chromatographic methods [2,9,5,10]. To achieve the necessary level of sensitivity, an enrichment step is needed before the chromatographic analysis. Historically, the initial extraction of OCPs from aqueous samples is performed batchwise (separatory funnel) or continuously using liquid–liquid extraction (LLE) [5,12]. Large volumes of both aqueous sample (typically, one litter) and high-purity organic extracting solvent (typically dichloromethane) are required, and most of the latter is ultimately discarded as chemically hazardous waste. Analytical methods that employ smaller volumes of initial sample and/or extracting solvent would be preferable. Procedures based on solid-phase extraction (SPE) permit the volumes of both the aqueous samples and extracting solvents to be reduced substantially. However, if the aqueous sample contained particle fines, both the small columns and disks employed were subjected to "plugging" [5].

Solid-phase microextraction (SPME) is a sample preparation technique, introduced by Pawliszyn and co-workers [13] that has received increasing attention, and is now widely accepted as a reliable technique. Thus, SPME has been applied to the determination of pesticide residue, such as organophosphorous pesticides (OPPs), nitrogen-containing pesticides and OCPs [9]. It has important advantages over conventional extraction techniques because it is solvent-free, fast, portable and easy to use. But SPME also suffers from some drawbacks: its fiber is fragile and has limited lifetime and the sample carry-over is also a problem [14,15].

Liquid-phase microextraction (LPME) has been developed as an alternative extraction technique [16–18]. This method provides analyte extraction using only a few microliters of organic solvent. LPME avoids some problems of the SPME method such as fiber degradation; it is also fast, inexpensive and uses very simple equipments. Moreover, although a variety of SPME fibers is commercially available, the choice of solvents for LPME is much broader and the organic phase is renewable at negligible cost [19]. In 2001, Zhao and Lee [20] described the application of LPME to the determination of OCPs in aqueous samples. Also, different formats of LPME have been utilized for OCPs extraction [21–24]. In our previous research, we demonstrated a new liquid phase microextraction technique based on utilizing a microdrop extractant that can be simply solidified at low temperatures [25,26]. The advantages of this method are its simplicity of operation, the small amount of solvent used, repeatability, low cost, and having very high preconcentration factors. The performance of the system is illustrated by determination of OCPs in water samples. The effects of various experimental parameters, such as the type of extraction solvent and its volume, extraction time, temperature and addition of salt were investigated and optimized. The efficiency of the presented method for analysis of real samples was tested.

2. Experimental

2.1. Reagents

All OCPs (lindane, heptachlor, aldrin, dieldrin, endrin, *p,p′*-DDE, DDD, *p,p′*-DDT, α-endosulfan, β-endosulfan, and methoxychlor) were purchased from Polyscience (New Haven, CT, USA). Pentachloronitrobenzene used as internal standard was obtained from Aldrich (Milwaukee, WI, USA). 1-Dodecanol (≥99%), reagent grade sodium chloride, HPLC grade methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). All water reagents used for preparation of aqueous solutions were purified with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Proper amount of each OCP was dissolved in 20 mL methanol to obtain a stock standard solution with a concentration of 200 mg L^{-1}. A fresh standard solution containing 11 OCPs with concentration of 2 mg L^{-1} was prepared in acetonitrile every week and stored at 4 °C. A solution of pentachloronitrobenzene (as internal standard) with concentration of 0.5 mg L^{-1} in 1-dodecanol was used as the extracting solvent.

2.2. Instrumentation

Separation, identification and quantification were carried out on a Chrompack CP-9001 (Chrompack, Middleburg, Netherlands) gas chromatograph system equipped with an electron capture detector. Helium and nitrogen (with 99.999% purity) were used as carrier (flow rate = 1 mL min^{-1}) and make-up gas (flow rate = 30 mL min^{-1}), respectively. The inlet was operated in the split mode with a split ratio of 1:15. Separation of OCPs was carried out using a CPSil8 CB fused silica capillary column (Chrompack, Middleburg, Netherlands) specialized for pesticides separation (50 m × 0.25 mm I.D., 0.25-μm film thickness). The injector and detector temperatures were set at 280 and 300 °C, respectively. The GC oven was kept at 50 °C for 5 min then raised to 200 °C at 10 °C min^{-1} and held for 5 min, finally raised to 250 °C at 5 °C min^{-1} and held for 10 min. The total run time was 40 min. All chromatograms were recorded and processed by the Maestro software, version 2.4. Stirring the solution was carried out with a magnetic heater-stirrer (Heidolph MR 3001 K). A simple water bath placed on the heater-stirrer was used for controlling the temperature of the sample solutions. All injections were car-

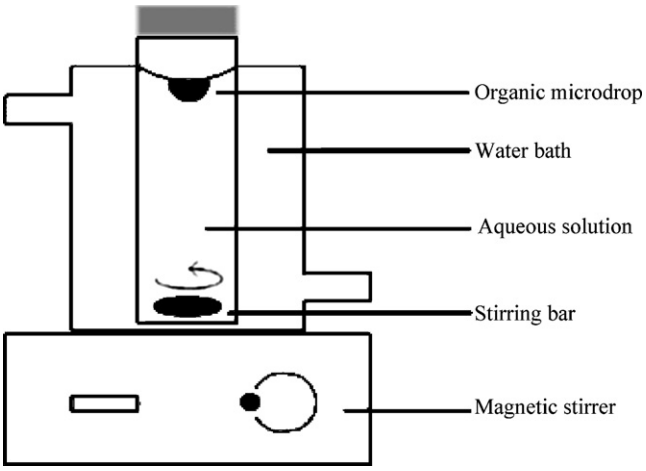

Fig. 1 – Schematic diagram of the proposed LPME apparatus.

ried out using a 10 μL model 701 N microsyringe (Reno, NV, USA).

2.3. *Analytical procedure*

Twenty milliliters of aqueous solution of OCPs (2 μg L^{-1}) were transferred into a 21 mL vial. A few microliters of 1-dodecanol were delivered to the surface of solution using the microsyringe. The vial was sealed and then the magnetic stirrer was turned on. Under the proper stirring conditions, the suspended droplet can remain in the top-center position of the aqueous sample. In an immiscible liquid–liquid system with the proper interface tension the microdroplet will not break up even in the absence of any support from the microsyringe's needle, polymer rod or other supporting material like hallow fibers. On the other hand, the movement of the microdroplet is affected by the flow field, which favors promotion of mass transfer inside the microdroplet (Fig. 1). After the desired extraction time, the sample vial was transferred into an ice beaker and the organic solvent solidified after 5 min. Then, the solidified solvent was transferred into a conical vial using a small spatula, and it melted immediately. Finally, 2 μL of extractant was injected into the gas chromatograph. All quantifications made in this study were based on the relative peak area of analyte to the internal standard (pentachloronitrobenzene) from the average of three replicate measurements. It is worthy to note that the solubility of 1-dodecanol in water is very low (0.004 g L^{-1} at 25 °C). Hence, the decrease of drop volume in each extraction period was about 0.1 μL.

3. Result and discussion

3.1. *Selection of extracting solvent*

The selection of extracting solvent is of major importance in LPME in order to obtain an efficient extraction. To choose a suitable organic solvent the following points should be considered. First, the chosen solvent should have high boiling point and low vapor pressure in order to reduce the risk of evaporation. Second, it should have good chromatographic behavior. Third, the partitioning coefficient of the analyte should be high [27]. Finally, it should have a melting point near the room temperature (in the range of 10–30 °C) [25]. According to these considerations, several extracting solvents, including 1-undecanol, 2-dodecanol, 1-dodecanol, *n*-hexadecane, 1-bromohexadecane, 1,10-dichlorodecane, and 1-chlorooctadecane were considered. Among different extracting solvents tested, 1-dodecanol showed the best extraction efficiency. Thus, 1-dodecanol was chosen as the extracting solvent in this investigation. In order to improve the precision and accuracy of the method, pentachloronitrobenzene was used as internal standard and added into the extracting solvent.

3.2. *Sample solution temperature*

Temperature is a major parameter affecting extraction efficiency. In most of LPME works, a temperature raise has led to higher enrichment factors [28]. This process facilitates mass transfer of the analyte from sample to the organic solvent and thus increases the efficiency of the extraction. The effect of sample solution temperature on the extraction efficiency was studied in the range of 30–70 °C by floating a 1-dodecanol microdrop for 35 min on the surface of the water samples. Experimental results (Fig. 2), clearly, showed that, by increasing the temperature, the extraction efficiency increased for all of the analytes. However, high temperatures (>65 °C) can lose the drop size dramatically and create over-pressurization in the sample vial which makes the extraction system unstable. Therefore, in further experiments the sample vial temperature was held at 65 °C.

3.3. *Effect of ionic strength*

Addition of salt to the sample may have several effects on the extraction efficiency for polar compounds. Extraction is usually enhanced by increasing salt concentration (salting-out effect). It was assumed that apart from the salting-out effect, the presence of salt causes a second effect and changes the physical properties of the Nernst diffusion film and thus

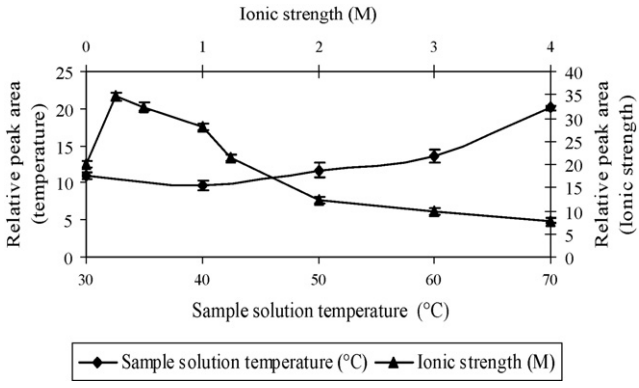

Fig. 2 – The effect of aqueous sample temperature and salt addition on the relative peak area. Conditions: extracting solvent volume: 10 μL; sample volume: 18 mL; stirring rate: 600 rpm; extraction time: 35 min.

reducing the rate of diffusion of the target analytes into the microdrop (salting-in effect) [29,30]. The effect of NaCl concentration (ranging from 0 to 4 M) was investigated and the extraction efficiency was monitored. The results, based on triplicate analysis, were presented in Fig. 2. According to the curves, it is clear that the addition of ionic strength increases the transport of the analytes to the extracting microdrop up to 0.25 M, but above 0.25 M, the salting-in effect was observed and the extraction efficiency for all further analytes decreased. Therefore, the NaCl concentration was adjusted at 0.25 M in all further experiments.

3.4. *Organic solvent volume*

For studying the effect of organic solvent volume on the analytical signal, some experiments were performed by increasing the microdrop volume from 4 to 14 μL. The results are shown in Fig. 3. As it was expected, an increase in the volume of the micro drop (up to 8 μL) resulted in a negligible increase in the extraction efficiency. However, at larger volumes, extraction efficiency decreased. By increasing the organic solvent volume both surface area and volume of organic drop were increased. The influence of organic solvent volume, therefore, originates from the integrated influence of two factors, justifying why the GC response enhances with increasing organic solvent volume up to 8 μL and decreases afterward [27].

3.5. *Effects of sample volume*

Sample volume plays an extremely important role in LPME analysis. It can influence the efficiency of convection and thus influences the extraction efficiency. In order to study the effect of sample volume on the extraction efficiency, some experiments were carried out using 21 mL vials and the volumes of samples were increased from 16 to 21 mL. The results showed that the largest analytical response was obtained at the sample volume of 20 mL (Fig. 3). By increasing the sample volume, the volume ratio of organic microdrop to sample decreases and preconcentration factor (PF) increases. Further increasing of sample volume to 21 mL resulted in the decreasing of the peak area. Because upon stirring the solution at a fixed rate, with a larger volume, the convection is not as good in the aqueous phase, resulting in less extraction [20,31,15,32]. Therefore, the volume of 20 mL was chosen as the optimal sample volume.

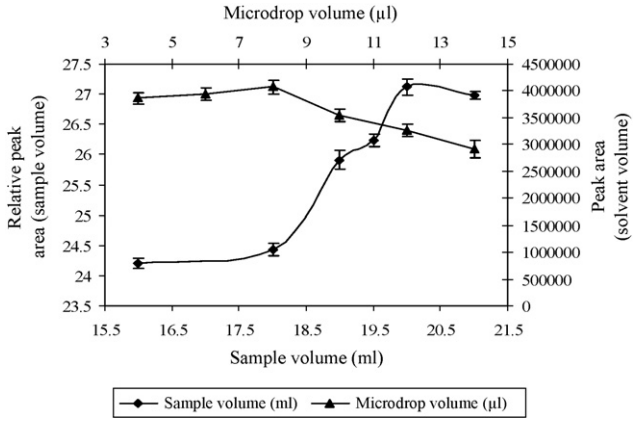

Fig. 3 – The effect of sample and extracting solvent volumes on the relative peak area. Conditions: sample solution temperature: 65 °C; stirring rate: 600 rpm; extraction time: 35 min and 0.25 M of NaCl.

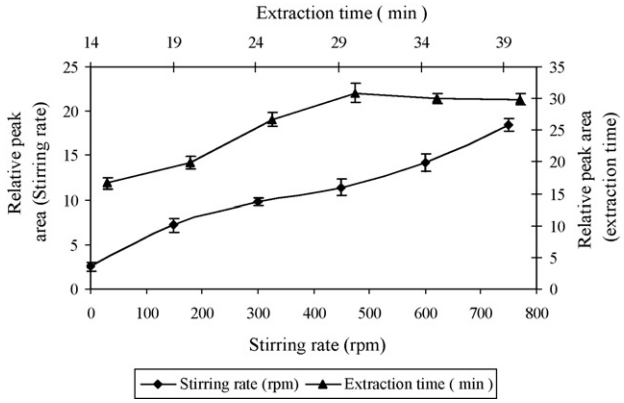

Fig. 4 – The effect of stirring rate and extraction time on the extraction efficiency. Conditions: sample solution temperature: 65 °C, extracting solvent volume: 8 μL; sample volume: 20 mL and 0.25 M of NaCl.

3.6. *Stirring rate*

A high stirring rate reduces the necessary time to reach thermodynamic equilibrium and thus increases extraction efficiencies significantly. Based on the film theory of convective-diffusive mass transfer for LPME system, at steady state, the aqueous phase mass-transfer coefficient increases with increasing stirring speed (rpm) because faster stirring speed can decrease the thickness of the diffusion film in the aqueous phase. As a consequence, agitation produces an enhancement in extraction efficiency [9,33,34]. The obtained results support this explanation. In this work, the samples with volumes of 20 mL were agitated at different stirring rates (0, 150, 300, 450, 600, and 750) with a 14 mm × 0.4 mm stirring bar on a stirrer plate. As shown in Fig. 4, the relative peak area of all analytes increases by increasing the stirring rate up to 750 rpm. Higher stirring rates (>800) were not used because of spattering, which damaged the microdrop. Hence, for further studies, a stirring rate of 750 rpm was chosen.

3.7. *Extraction time*

Like SPME, LPME is not an exhaustive extraction method under the real conditions and for optimum repeatability of the extraction, it is necessary to choose an extraction time during which equilibrium between aqueous and organic phase is reached. The amount of analyte extracted at a given time depends upon the mass transfer of analyte from the aqueous phase to the organic phase. This procedure requires a period of time for equilibrium to be established. Normally, the time for establishing equilibrium is selected as the extraction time [20]. The effect of time was examined in the range

of 15–40 min at the optimized experimental conditions. The relative peak areas increased with extraction time up to 30 min (Fig. 4). After 30 min, the extraction system basically reached a steady state and no dramatic increase in relative peak areas was observed with additional extraction time. Therefore, extraction time period of 30 min was chosen to obtain a reasonable sensitivity. Although the extraction time was relatively long, the sheer smallness of the developed LPME system makes parallel extraction a most attractive. In the present work five samples were extracted together, but much higher parallelization is feasible when using a multi stirrer.

3.8. Evaluation of the method performance

A chromatogram of the standard solution of analytes at 2 μg L^{-1} concentrations after utilizing the proposed method with an 8 μL microdrop of 1-dodecanol containing 0.5 mg L^{-1} of pentachloronitrobenzene was shown in Fig. 5. Calibration curves were drawn using 10 spiking levels of OCPs in the concentration range of 25–2000 ng L^{-1}. For each level three replicate extractions were performed at optimal conditions (extraction time: 30 min, drop volume: 8 μL, stirring rate: 750 rpm, sample temperature: 65 °C, sample volume: 20 mL and ionic strength: 0.25 M of NaCl). The corresponding regression equations, correlation coefficients (r^2), dynamic linear ranges (DLRs) and the limit of detections (LODs), based on, three times of signal to noise ratio, were calculated and summarized in Table 1. In order to examine the preconcentration factor of each analyte, a series of standard solutions (at concentration of 50, 100, 200, 300, 500, 700, 1000, 2000, and 5000 μg L^{-1}) in 1-dodecanol were prepared and 2 μL of them were injected into GC. Then the plots of relative peak area against the concentration of each analyte were drawn. The PF was calculated as the slope ratio of LPME calibration curve to that of the non-extraction curve and the calculations are summarized in Table 1. In addition, the percentages of extractions of analytes were evaluated. Three replicate extractions from a spiked sample containing 2 μg L^{-1} of each OCP were performed and the percentage of extraction for each analyte

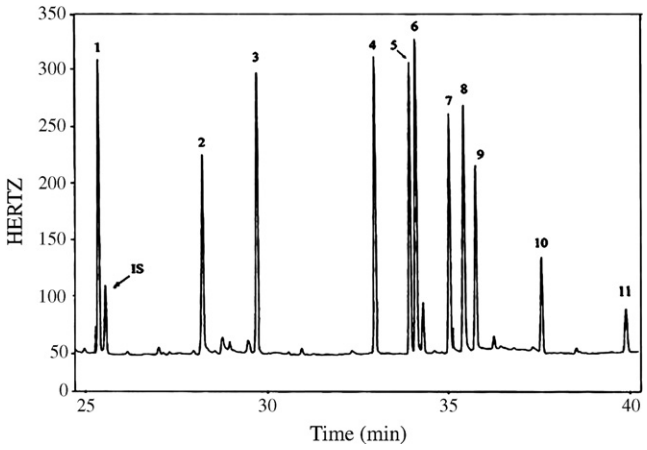

Fig. 5 – Chromatogram of 2 μg L^{-1} standard solution of OCPs after extraction with proposed method. The column temperature was raised from 50 °C (5 min, initial temperature) to 200 °C (5 min) at 10 °C min^{-1}, then to 250 °C (10 min, final temperature) at 5 °C min^{-1}. (1) Lindan; (IS) pentachloronitrobenzene (internal standard); (2) heptachlor; (3) aldrin; (4) α-endosulfan; (5) *p,p′*-DDE; (6) dieldrin; (7) endrin; (8) β-endosulfan; (9) DDD; (10) *p,p′*-DDT; (11) methoxychlor.

calculated based on the following equation and summarized in Table 1.

$$\text{Extraction}\,(\%) = \frac{C_{eq}^{org} V^{org}}{C_{\circ}^{aq} V^{aq}} \times 100$$

It is obvious that after a single step extraction using 8 μL of organic solvent 28.3–53.5% of OCP was transferred into the organic microdrop.

3.9. Real water analysis

To assess the applicability of the method to real samples, the proposed method was applied to the extraction and determination of OCPs from real water samples. Three water samples;

Table 1 – Figures of merit of the proposed LPME-GC-ECD method for extraction and determination of OCPs

No.	Analyte	LOD[a] (ng L^{-1})	r^2	Regression equation	DLR (ng L^{-1})	RSD% (n = 5)	PF[b]	Extraction efficiency (%)
1	Lindan	11	0.9962	A_r[c] = 0.004C + 0.1398	50–2000	5.8	1311	52.4
2	Heptachlor	8	0.9968	A_r = 0.003C − 0.0116	50–750	6.1	1198	47.9
3	Aldrin	7	0.9996	A_r = 0.0048C − 0.0236	50–750	5.4	708	28.3
4	α-Endosulfan	16	0.9975	A_r = 0.0045C + 0.0258	25–750	5.5	1267	50.7
5	*p,p′*-DDE	10	0.9984	A_r = 0.00038C − 0.118	50–2000	6.3	986	39.4
6	Dieldrin	19	0.9986	A_r = 0.0048C + 0.0086	75–2000	6.4	1290	51.6
7	Endrin	14	0.9989	A_r = 0.0039C − 0.0701	25–2000	7.2	1337	53.5
8	α-Endosulfan	9	0.9968	A_r = 0.0051C − 0.1121	50–2000	5.9	1091	43.6
9	DDD	8	0.9931	A_r = 0.0031C − 0.019	50–2000	4.9	884	35.4
10	*p,p′*-DDT	16	0.9992	A_r = 0.0032C − 0.1619	75–750	5.5	1190	47.6
11	Methoxychlor	15	0.9976	A_r = 0.002C − 0.0226	50–750	5.9	1262	50.5

[a] LOD was calculated as the signal to noise ratio of 3.
[b] Preconcentration factor.
[c] Relative peak area of analyte to internal standard.

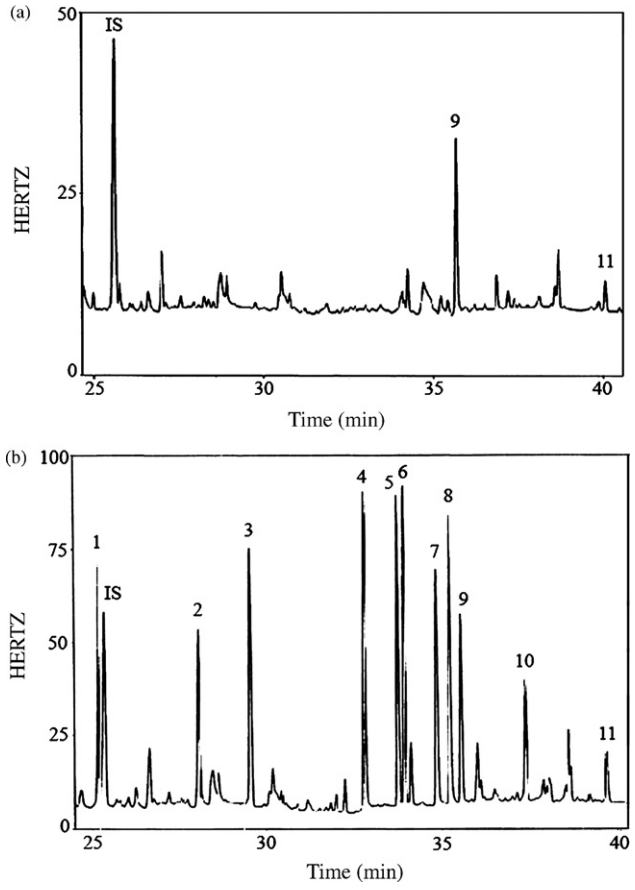

Fig. 6 – Chromatograms of (a) agricultural water and (b) spiked agricultural water at concentration level of 500 ng L^{-1} obtained by using proposed LPME method combined with GC-ECD. (1) Lindan; (IS) pentachloronitrobenzene; (2) heptachlor; (3) aldrin; (4) α-endosulfan; (5) *p,p′*-DDE; (6) dieldrin; (7) endrin; (8) β-endosulfan; (9) DDD; (10) *p,p′*-DDT; (11) methoxychlor.

river (Tajan, Iran), agricultural water (Rey, Tehran, Iran) and tap water (Tarbiat Modares University) were selected to check the accuracy of the proposed method. River and agricultural water samples were collected in glass bottles. Tap water sample was collected after allowing the water to flow for 14–15 min. All of water samples were stored in a fridge at 4 °C till analysis time. Water samples were filtered before analysis, using 0.45 μm cellulose acetate membrane filter to eliminate particulates. The results for tap and river water showed that they were free of OCP contamination. In the agricultural water sample, DDD and methoxychlor were detected. The LPME–GC-ECD chromatograms obtained for agricultural water before and after spiking with 500 ng L^{-1} of OCPs are shown in Fig. 6. The concentration of DDD and methoxychlor in the agricultural water, were 180 ng L^{-1} (RSD% = 5.3) and 112 ng L^{-1} (RSD% = 7.2) respectively. The existence of DDD and methoxychlor in agricultural water was confirmed using GC–MS (Fig. 7). River, tap and agricultural water were spiked with OCPs standards to assess matrix effects. Results are shown in Table 2. The data has shown that the relative errors for determination of OCPs

Table 2 – The results obtained from analysis of real samples

Analyte[a]		1	2	3	4	5	6	7	8	9	10	11
River water (Tajan, Iran): spiked concentration of OCPs: 100 ng L^{-1}	Concentration (ng L^{-1})	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Found (ng L^{-1})	95.5	93.7	89.1	100.4	91.9	96.4	98.0	110.1	107.0	94.6	92.5
	Relative error%	−4.5	−6.3	−10.9	0.4	−8.1	−3.6	−2	10.1	7	−5.4	−7.5
	RSD% (*n* = 4)	6.9	7.6	5.2	5.9	8.2	7.3	8.4	7.4	6.6	5.8	8.7
Tap water (Tehran, Iran): spiked concentration of OCPs: 300 ng L^{-1}	Concentration (ng L^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Found (ng L^{-1})	311.1	289.1	295.6	288.4	306.7	302.2	290.8	294.6	310.6	287.0	291.5
	Relative error%	3.7	−3.6	−1.5	−3.9	2.2	0.7	−3.1	−1.8	3.5	−4.3	−2.8
	RSD% (*n* = 4)	4.9	5.7	8.6	8.2	5.9	6.6	7.9	5.8	6.9	7.8	6.2
Agricultural water (Rey, Tehran, Iran): spiked concentration of OCPs: 500 ng L^{-1}	Concentration (ng L^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	180	ND	112
	RSD% (*n* = 4)	–	–	–	–	–	–	–	–	5.2	–	6.8
	Found (ng L^{-1})	514.1	491.0	542.9	488.3	494.9	509.2	486.3	521.7	648.1	481.5	627.0
	Relative error%	2.8	−1.8	8.6	−2.3	−1	1.8	−2.7	4.3	−6.4	−3.7	3.0
	RSD% (*n* = 4)	8.4	5.3	7.5	9.1	8.4	6.9	7.8	9.3	5.9	6.3	7.2

[a] Analytes 1–11 were defined in Table 1.
[b] Not detected.

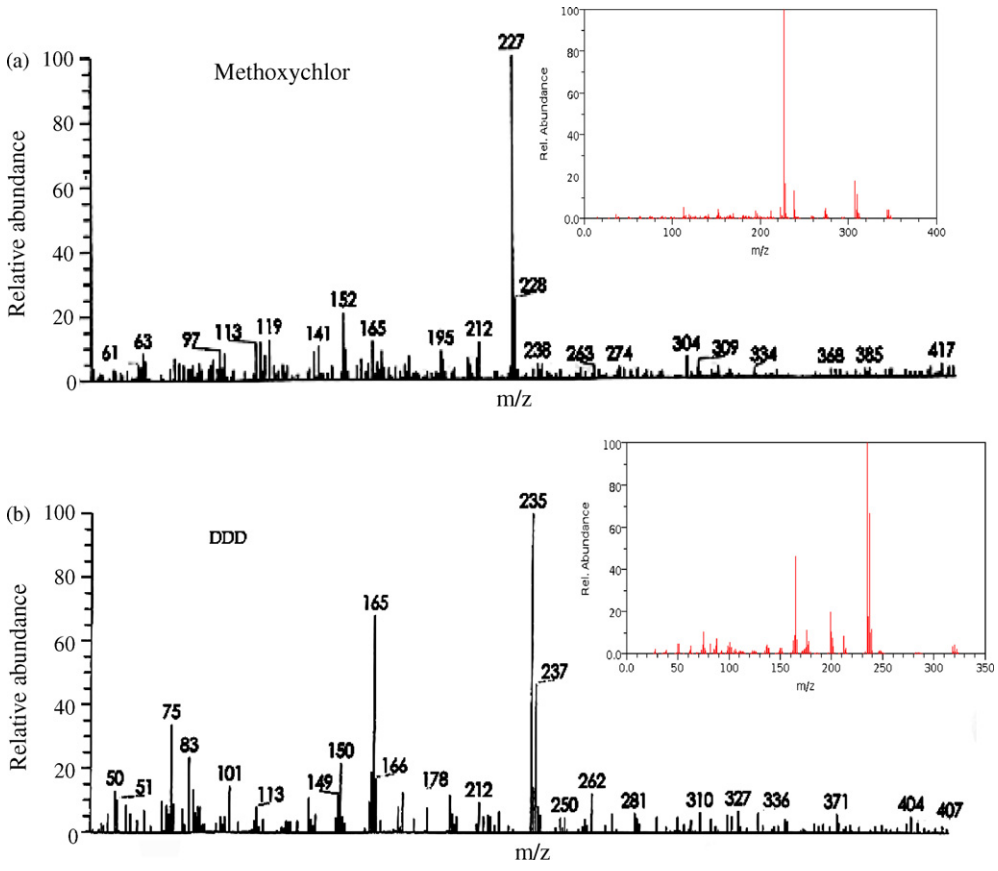

Fig. 7 – Mass spectra of detected compounds in agricultural water: (a) methoxychlor and (b) DDD. *Note:* Inset on the top right of main figures represents reference mass spectra [35]. (For interpretation of the references to colour in the artwork, the reader is referred to the web version of the article.)

were in the range of −10.9 to +10.1%. These results demonstrate the suitable capability of the proposed method for determination of OCPs in different water samples with various matrices.

4. Conclusion

This paper has outlined the successful development and application of a method based on the LPME technique combined with capillary GC-ECD for the analysis of OCPs in water samples. Compared to conventional sample preparation methods such as LLE and SPE. the current method has numerous advantages such as: simplicity, low cost, ease of operation, no possibility of sample carry-over and short analysis time. Good linearity (25–2000 ng L^{-1}), high sensitivity and repeatability ($4.9 < RSDs < 7.2\%$) of results were obtained. In addition, the method requires only small volume of organic extractants; therefore it is an environment friendly approach to the LPME. The performances of this procedure for the extraction of OCPs from different water with various matrices were excellent.

Acknowledgment

This work was supported by a grant from the Iran National Science Foundation, INSF (Grant No. 86023/06).

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