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ORIGINAL

Homogeneous Liquid–Liquid Microextraction for Determination of Organochlorine Pesticides in Water and Fruit Samples

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Abstract A fast and effective preconcentration method for extraction of organochlorine pesticides (OCPs) was developed using a homogeneous liquid–liquid extraction based on phase separation phenomenon in a ternary solvent (water/methanol/chloroform) system. The phase separation phenomenon occurred by salt addition. After centrifugation, the extraction solvent was sedimented in the bottom of the conical test tube. The OCPs were transferred into the sedimented phase during the phase separation step. The extracted OCPs were determined using gas chromatography–electron capture detector. Several factors influencing the extraction efficiency were investigated and optimized. Optimal results were obtained at the following conditions: volume of the consolute solvent (methanol), 1.0 mL; volume of the extraction solvent (chloroform), 55 μL; volume of the sample, 5 mL; and concentration of NaCl, 5 % (w/v). Under optimal conditions, the preconcentration factors in the range of 486–1,090, the dynamic linear range of 0.01–100 μg L^{-1}, and the limits of detection of 0.001–0.03 μg L^{-1} were obtained for the OCPs. Using internal standard, the relative standard deviations for 1 μg L^{-1} of the OCPs in the water samples were obtained in the range of 4.9–8.6 % ($n = 5$). Finally, the proposed method was successfully applied for extraction and determination of the OCPs in water and fruit samples.

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Introduction

Most organochlorine pesticides (OCPs) are persistent organic pollutants (POPs) in the environment. Nine of the OCPs were the subjects of the Stockholm convention on POPs. The proposed treaty called for urgent global actions to reduce and eliminate the release of these compounds [1]. They are a possible risk to the environment because of their toxicity and ability to bioaccumulate. Studies involving determination of OCPs in environmental matrices often deal with samples with low analyte concentrations containing a high number of interfering compounds. Thus, simple and highly efficient extraction and preconcentration methods are required to detect trace levels of pollutants in water samples.

OCPs can be extracted from aqueous matrices using a variety of conventional techniques including liquid–liquid extraction (LLE) [2] and solid-phase extraction (SPE) [3]. These techniques, whilst offering excellent recovery and analytical precision of OCPs, are also time consuming, expensive, and especially in relation to LLE, hazardous to health due to the high volume of toxic solvents used [4]. Although SPE consumes much less time than LLE, a solvent evaporation step before final analysis is required [5]. Solid-phase microextraction (SPME), a fast and solvent-free technique, overcomes the above problems [6]. However, it has also some drawbacks such as high cost, sample carry-over, and a decline in performance with time [7]. Recently, a solvent-minimized sample pretreatment procedure, known as liquid-phase microextraction (LPME), has

gained lots of attentions [8–10]. This technique is inexpensive and there is minimal exposure to toxic organic solvents. The major problem with the technique is that the microdrop suspended on the microsyringe needle is easily dislodged during stirring of the aqueous sample. However, selection of a syringe with a beveled needle tip and a very small volume of solvent can obviate this difficulty.

On the other hand, homogenous liquid–liquid microextraction (HLLE), which is one of the LPME modes, reduces the extraction time, cost, consumption and exposure to the organic solvent. This method extracts the solute from a homogeneous solution into a very small sedimented phase formed from the solution by the phase separation phenomenon. In HLLE, there are no interfaces between the water consolute and the extracting solvent. In other words, the interface surface area is infinitely large. Accordingly, no vigorous mechanical shaking is necessary. The procedure is simple and requires only addition of the reagent [11–13]. The ternary component solvent system and the perfluorinated surfactant system are the two usual modes of homogeneous liquid–liquid extraction [14]. Recently, homogeneous liquid–liquid extraction has been successfully utilized for extraction of some organic and inorganic analytes including mononitrotoluenes, and ferric and molybdenyl ions [14–16]. The objective of this research was to investigate preconcentration and determination of OCPs by HLLE coupled to gas chromatography–electron capture detector (GC–ECD) in water and fruit samples. The effects of various experimental parameters on extraction of OCPs from water samples were investigated. The effective parameters on the HLLE efficiency were considered and optimized.

Experimental Setup

Reagents and Materials

All OCPs (α-BHC, β-BHC, γ-BHC, heptachlor, δ-BHC, aldrin, heptachlor epoxide, γ-chlordane, α-chlordane, α-endosulfan, 4,4′-DDE, dieldrin, endrin, 4,4′-DDD, β-endosulfan, endrin aldehyde, 4,4′-DDT, endosulfan sulfate, and methoxychlor) were purchased from Aldrich (Milwaukee, WI, USA). Acetonitrile, methanol, chloroform, sodium chloride, and PCB 9 (internal standard) were of the highest purity available from Merck (Darmstadt, Germany). Ultrapure water was purified on a Milli-Q water purification system from 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 OCPs with concentration of 2 mg L^{-1} was prepared in acetonitrile every week and stored at 4 °C. A solution of PCB 9 (as internal standard) with concentration of 10 mg L^{-1} in chloroform was used as the extracting solvent.

GC–ECD Analysis for Quantification

GC–ECD was applied for both determination and quantification of OCPs in the extracted samples. Pretreated samples were analyzed on the chromatographic system including a Chrompack CP 9000 gas chromatograph (Middleburg, the Netherlands) equipped with an ECD and a Chrompack CP-Sil 8 CB fused-silica capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness). Carrier gas (N_2) was set at the flow rate of 0.5 mL min^{-1}. During the whole analysis, the injector was operated in the split mode with an injector temperature of 260 °C. The oven temperature was initially set at 100 °C (2 min hold), followed by a temperature ramp of 6 °C min^{-1} to 280 °C, and held for 10 min. The analytical signal was taken as the ratio of analyte peak area to that of the internal standard.

Homogeneous Liquid–Liquid Extraction Procedure

For the HLLE, a 5-mL sample solution containing 50 μg L^{-1} OCPs was placed in a 10-mL screw cap test tube with conic bottom. Then, 1.0 mL methanol (as consolute solvent) containing 55 μL chloroform (as extracting solvent) was added into the sample solution and the mixture was gently shaken by hand (accordingly, no vigorous mechanical shaking was necessary). Under these conditions, a homogeneous solution was obtained. By adding 0.25 g NaCl into the solution and shaking, a cloudy mixture was formed in the test tube. The cloudy mixture was centrifuged for 3 min at 3,500 rpm. Accordingly, fine particles of the extraction phase were sedimented in the bottom of the conical test tube. Volume of the sedimented phase was about 10.0± 0.5 μL. 2 μL of the sedimented phase was taken into a 10-μL microsyringe and injected into the GC.

Preparation of Real Samples

The real water samples collected were stored in pre-cleaned polyethylene bottles in a fridge at about 4 °C under darkness condition. The samples were filtered through a 0.45-μm pore-size cellulose acetate membrane filter prior to extraction.

Fruit samples were homogenized and 2 g of the samples accurately were weighed and put into a 10-mL centrifuge tube, to which 2.0 mL methanol was added. The resultant samples were ultrasonically extracted for 2 min, with output control knob set at full power and with mode switch on pulse (energy on 50 % of time and off 50 % of time). After the sonication, the extracts were centrifuged at 5,000 rpm for 5 min and the supernatant liquid was passed through PTFE syringe filter (13 mm, 0.22 μm) to remove particles. The resulting solution was subjected to HLLME process.

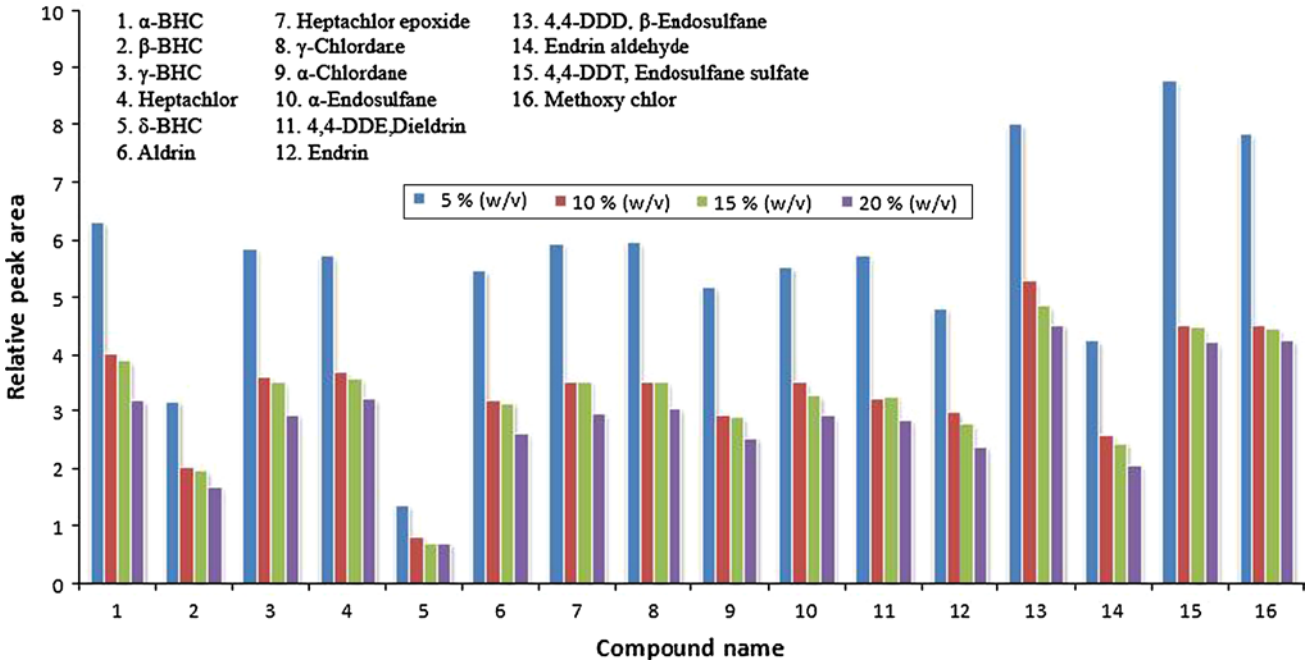

Fig. 1 Effect of NaCl concentration on extraction recovery of OCPs

Results and Discussion

Method Development

In the present research, the optimization process was carried out using one-variable-at-a-time method. In order to obtain the optimal conditions for HLLE of OCPs from water samples, the effects of different parameters such as extracting solvent volume, consolute solvent volume, NaCl concentration, and extraction time on the extraction efficiency were evaluated and optimized. In order to achieve good sensitivity, precision, and selectivity for extraction and determination of OCPs, selection of an appropriate solvent for HLLE process is of great importance. The extracting solvent has to meet three requirements: to extract the analytes well, to separate well from the analytes peaks in the chromatogram, and to have density higher than water. Since chloroform has suitable conditions in this regard and was readily sedimented in the bottom of the conic tube, it was selected as the extracting solvent.

Selection of Consolute Extractant

Miscibility of consolute solvent with the extracting solvent and aqueous phase is the main point for selection of the consolute solvent. Thereby, acetonitrile and methanol were considered for this purpose. The results showed the same percentage of recoveries for the analytes in the presence of both solvents. Methanol was selected as the consolute solvent in the subsequent extractions because of its availability and low cost.

Effect of Phase Separator Reagent Concentration

In HLLE process, a homogeneous solution is formed under initial conditions, and then water-immiscible chloroform is separated from aqueous solution due to addition of NaCl. The rate of phase separation phenomenon and the volume of sedimented chloroform depend on NaCl concentration. In order to investigate the optimal amount of NaCl in the quantitative HLLE of OCPs, the experiments were carried out by changing the NaCl concentration in the sample solution in the range of 5–20 % w/v. As shown in Fig. 1, salt addition promotes transportation of analytes into the organic phase; so the highest extraction recovery was obtained at NaCl concentration 5 % w/v. At higher percentages of NaCl, a decrease in signal occurred due to increasing of the sedimented phase volume and dilution effect. Consequently, preconcentration factor of the analytes decreased. Therefore, to create the sedimented phase, 5 % w/v NaCl was added into the homogenous solution in the subsequent studies.

Effect of Extraction Solvent Volume

To study the effect of the extracting solvent volume, the solutions containing different volumes of chloroform were subjected to the same HLLE procedure. The experimental conditions were fixed and included the use of different volumes of chloroform in the range of 50–65 μL. The results are illustrated in Fig. 2. It was also found that the volume of sedimented phase in the bottom of the test tube was

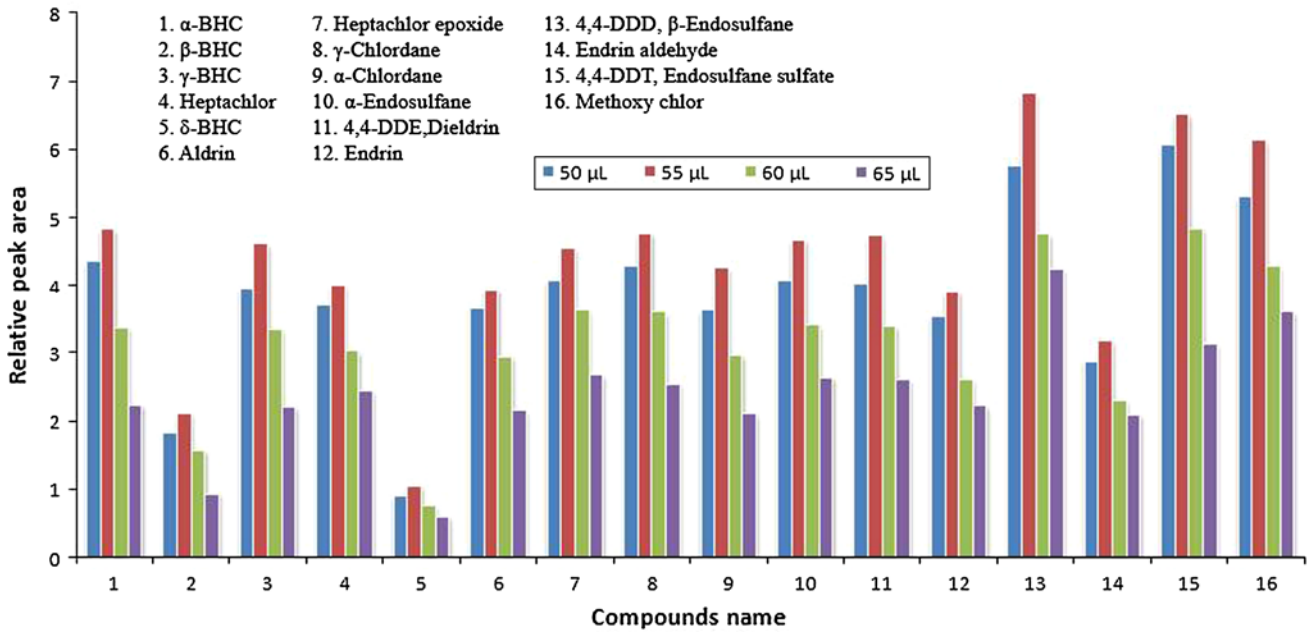

Fig. 2 Effect of extraction solvent volume on extraction recovery of OCPs

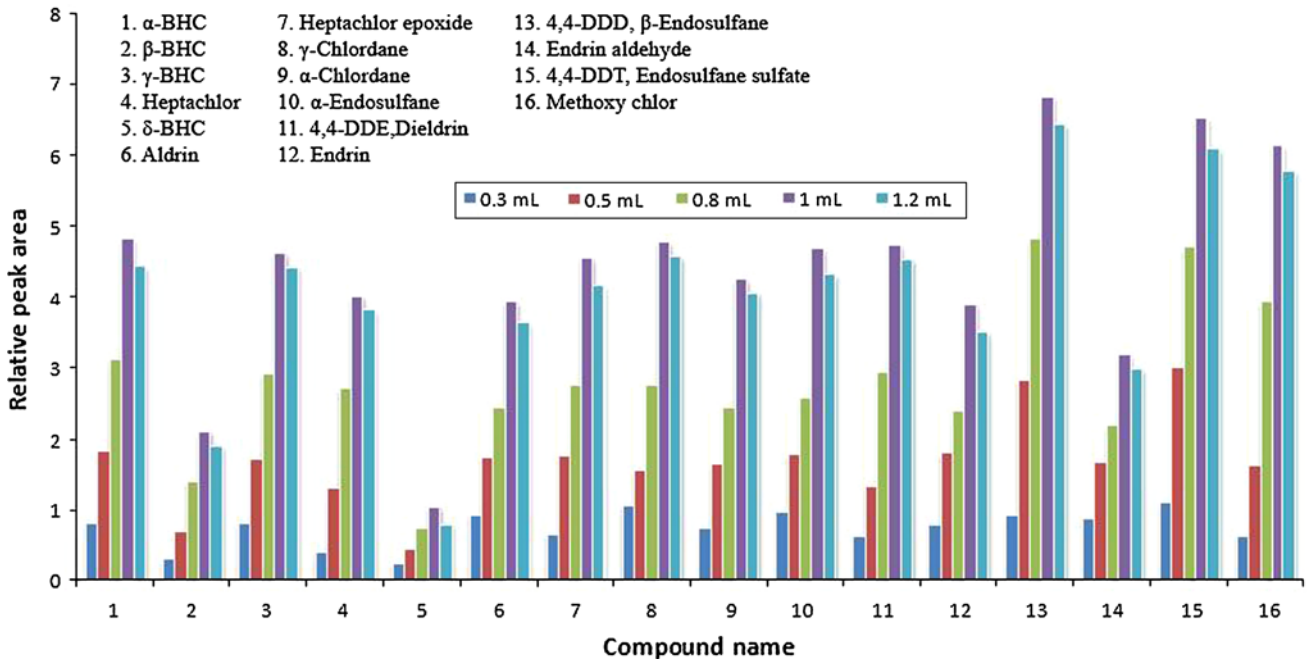

Fig. 3 Effect of consolute solvent volume (methanol) on extraction recovery of OCPs

increased from 5.0 to 20.0 µL by increasing the volume of chloroform from 50 mL to 65 µL. Extraction efficiencies were increased by increasing the volume of chloroform up to 55 µL. At higher volumes of chloroform, due to increasing of sedimented phase volume and dilution of the OCPs, GC peak areas of the analytes decreased. Thus, 55 µL chloroform was used in further experiments.

Effect of Consolute Solvent Volume

The effect of methanol volume as consolute solvent on the extraction efficiency was investigated in the range of 0.3–1.2 mL. Figure 3 shows that the extraction recoveries increase with the increasing methanol volume up to 1.0 mL. In the presence of 1.2 mL methanol, the extraction

Table 1 Figures of merit of the proposed HLLE for extraction and determination of OCPs

Analyte	LR (ng mL^{-1})	LOD (ng mL^{-1})[a]	LOD (μg kg^{-1})[b]	r^2	PF	RSD% ($n = 5$)
α-BHC	0.01–100	0.005	0.01–0.03	0.9989	630	6.6
β-BHC	0.05–100	0.01	0.03–0.05	0.9997	616	5.7
γ-BHC	0.01–100	0.005	0.008–0.01	0.9990	584	5.1
Heptachlor	0.03–100	0.008	0.01–0.03	0.9994	573	7.2
δ-BHC	0.05–60	0.03	0.05–0.1	0.9942	486	4.9
Aldrin	0.03–60	0.008	0.01–0.03	0.9963	1090	7.8
Heptachlor epoxide	0.01–100	0.005	0.008–0.01	0.9971	592	7.6
γ-Chlordane	0.01–100	0.005	0.008–0.01	0.9949	594	7.6
α-Chlordane	0.03–80	0.008	0.01–0.03	0.9970	508	5.5
α-Endosulfan	0.03–60	0.008	0.01–0.03	0.9980	551	6.8
4,4′-DDE, dieldrin	0.03–80	0.005	0.01–0.03	0.9980	572	8.5
Endrin	0.05–60	0.01	0.03–0.05	0.9984	960	8.0
4,4′-DDD, β-endosulfan	0.01–60	0.001	0.005–0.01	0.9990	835	7.6
Endrin aldehyde	0.05–60	0.01	0.03–0.05	0.9994	533	8.6
4,4′-DDT, endosulfane sulfate	0.01–60	0.002	0.008–0.02	0.9992	876	8.1
Methoxychlor	0.01–60	0.005	0.008–0.01	0.9998	774	6.9

[a] LODs were obtained in aqueous solution

[b] LODs were obtained in fruit samples

Table 2 Comparison of the proposed method with other methods applied for extraction and determination of OCPs

Method	LOD (μg L^{-1})	Analysis time (min)	LR (μg L^{-1})	RSD%	References
SDME–GC–MS	0.05–0.5	30	0.05–50	<18.9	[17]
SPME–GC–ECD	0.0006–0.021	30	0.025–50,000	<28	[18]
HF–LPME–GC–MS	0.013–0.059	30	5–100	<14.0	[19]
DLLME-GC–MS	0.001–0.025	5	0.5–16	<15	[20]
SFDME–GC–ECD	0.007–0.019	30	0.02–2	<7.2	[21]
SPE–GC–ECD	0.3–15	–	10–500	–	[22]
ASE[a]–SPME–GC–MS	0.5–6	–	–	4–31	[23]
HLLE–GC–ECD	0.001–0.03	5	0.01–100	<8.6	Present method

[a] Accelerated solvent extraction (ASE)

recoveries decreased because of the decrease in the sedimented phase volume and using higher volumes of methanol (>1.2 mL), no sedimented phase was obtained in the presence of NaCl. Also in the presence of lower volumes of methanol (<0.3 mL), no homogeneous solution was formed. Thus, 1 mL methanol was chosen for further studies.

Effect of Extraction Time

Extraction time is one of the most important factors in most extraction procedures, especially in microextraction methods such as SPME and LPME. In HLLE, the profile of extraction time was studied by monitoring the variation of relative peak areas of analytes with the time of cloudy state before starting centrifugation. The effect of time was examined in the range of 0–30 min under optimal extraction conditions. The results showed that extraction time has no influence on extraction efficiency. It is clear that the surface area between the extracting solvent and the aqueous phase is infinitely large. Therefore, transfer of the analytes from aqueous phase to extraction phase is fast. This is the most important advantage of HLLE technique.

According to the overall results of optimization study, the following experimental conditions were chosen: consolute solvent, 1 mL methanol; extraction solvent, 55 μL chloroform; and phase separator reagent, 5 % w/v NaCl.

Evaluation of Method Performance

Main Method Parameters

For quantitative analysis of OCPs, a calibration curve at six different concentration levels of the analyte obtained by spiking the standards directly into distilled water was

Table 3 Analytical results for determination of OCPs in real samples

Compounds	Tap water		Grape		Nectarine		Orange		Pineapple	
	Detected ($\mu g\ L^{-1}$)	Recovery[a] (%) ±SD ($n = 3$)	Detected ($\mu g\ kg^{-1}$)	Recovery (%) ±SD ($n = 3$)	Detected ($\mu g\ kg^{-1}$)	Recovery (%) ±SD ($n = 3$)	Detected ($\mu g\ kg^{-1}$)	Recovery (%) ±SD ($n = 3$)	Detected ($\mu g\ kg^{-1}$)	Recovery (%) ±SD ($n = 3$)
α-BHC	ND	96.3 ± 5.9	3.6	92.6 ± 8.3	ND	86.5 ± 11.4	3.0	91.7 ± 10.7	ND	84.4 ± 12.5
β-BHC	ND	98.5 ± 6.2	ND	94.9 ± 9.6	ND	90.4 ± 13.2	ND	88.5 ± 11.2	ND	80.7 ± 13.8
γ-BHC	ND	98.4 ± 5.5	ND	84.5 ± 9.0	ND	82.7 ± 12.6	ND	95.0 ± 10.5	ND	82.5 ± 12.3
Heptachlor	ND	105.0 ± 6.8	ND	83.8 ± 10.2	ND	85.0 ± 14.9	ND	76.2 ± 13.7	ND	84.0 ± 15.9
δ-BHC	ND	96.8 ± 5.2	ND	79.5 ± 8.5	ND	95.9 ± 10.5	ND	82.2 ± 8.5	ND	75.5 ± 10.6
Aldrin	ND	100.9 ± 6.0	ND	87.4 ± 7.9	ND	79.4 ± 9.2	ND	78.5 ± 8.0	ND	78.1 ± 9.9
Heptachlor epoxide	ND	105.7 ± 6.8	ND	90.0 ± 11.4	ND	89.2 ± 15.8	ND	85.5 ± 14.2	ND	81.6 ± 16.2
γ-Chlordane	ND	98.5 ± 5.9	ND	87.0 ± 9.3	ND	93.8 ± 10.8	ND	92.6 ± 9.6	ND	84.4 ± 11.4
α-Chlordane	ND	95.9 ± 5.2	ND	75.8 ± 8.8	5.4	80.7 ± 10.5	2.0	86.3 ± 9.1	ND	92.8 ± 10.4
α-Endosulfan	ND	92.4 ± 4.7	ND	88.5 ± 7.2	ND	86.5 ± 8.9	ND	86.1 ± 6.3	ND	89.0 ± 9.0
4,4′-DDE, dieldrin	ND	99.1 ± 6.8	ND	79.4 ± 9.5	ND	86.7 ± 11.0	ND	83.9 ± 11.4	ND	85.2 ± 14.3
Endrin	ND	104.6 ± 7.4	ND	92.0 ± 14.0	ND	94.0 ± 13.3	ND	88.4 ± 12.7	2.7	88.4 ± 15.7
4,4′-DDD, β-endosulfan	ND	98.0 ± 6.5	ND	76.1 ± 9.6	ND	89.2 ± 14.5	ND	92.5 ± 14.0	ND	90.0 ± 14.9
Endrin aldehyde	ND	94.8 ± 6.4	ND	85.5 ± 10.3	ND	78.5 ± 14.9	ND	82.9 ± 13.6	ND	79.8 ± 13.3
4,4′-DDT, endosulfan sulfate	ND	98.5 ± 7.7	14.2	95.0 ± 9.8	104.0	91.6 ± 11.4	ND	86.5 ± 10.2	ND	115.3 ± 11.5
Methoxychlor	ND	102.7 ± 6.5	ND	90.2 ± 10.8	ND	87.0 ± 12.6	ND	84.5 ± 10.9	ND	89.1 ± 12.4

[a] The spiked concentrations are 10 ng g^{-1} of OCPs

plotted. Performance of the method under optimal conditions is shown in Table 1. Linearity was observed over the range of 0.01–100 ng mL^{-1} for most OCPs, with the coefficient of determination (r^2) in the range of 0.9942–0.9998. The limits of detection (LODs), calculated as concentration equivalent to three times of standard deviation of the blank divided by the slope of calibration curve, were in the range of 0.001–0.03 μg L^{-1} and 0.005–0.1 μg L^{-1} for different OCPs in water and fruit samples, respectively. Precision of the method was calculated by five replicates of extraction and determination of OCPs at 1 μg L^{-1} level, and the relative standard deviations (RSDs) in the range of 4.9–8.6 % were obtained. The preconcentration factor (PF), calculated as the ratio of the final concentration of analyte in the sedimented phase and its concentration in the initial solution, was in the range of 486–1,090 for 5.0 mL sample solution.

A comparison between the figures of merit of the proposed method and some of the published methods for extraction and determination of OCPs is summarized in Table 2. Clearly, the proposed method has a good sensitivity and precision with a suitable dynamic linear range. Also, the LODs obtained for the analytes by the present method with sample volume of 5 mL at very short extraction time are better than those obtained by other methods.

Application of the Proposed Method for Real Samples

To evaluate the applicability of the proposed method for extraction and determination of the analytes in real samples, extraction and determination of the OCPs in various tap water and fruit samples were performed.

Analysis of Water Samples

Two aqueous samples were collected from tap water of Tarbiat Modares University (Tehran, Iran) in two seasons, of winter and spring. To assess the matrix effects, the water samples were spiked with OCPs standards at a concentration of 10 μg L^{-1}. Table 3 shows that the results of three replicate analysis of each water sample obtained by the proposed method are in satisfactory agreement with the added amounts of OCPs.

Extraction of OCPs from Fruit Samples

The proposed method combined with ultrasonic-assisted extraction was applied to extract the OCPs from complex matrices. Fresh fruits (grape, nectarine, orange, and pineapple) were cut into small pieces and an aliquot of 2.0 g was extracted by 2 mL methanol in ultrasonic bath for 40 min. After the sonication, the extracts were centrifuged at 5,000 rpm for 5 min and the supernatant liquid was decanted. For HLLE, a 1-mL aliquot of the residual extract along with 55 μL chloroform was placed in a 5-mL sample vial and 5 mL ultrapure water was added. Then, the sample was subjected to HLLE as described previously. The relative recoveries and reproducibilities were evaluated by spiking OCPs standards in homogenous fruit samples at the concentration of 10 ng g^{-1} using the presented method (Table 3). The relative recoveries of the method

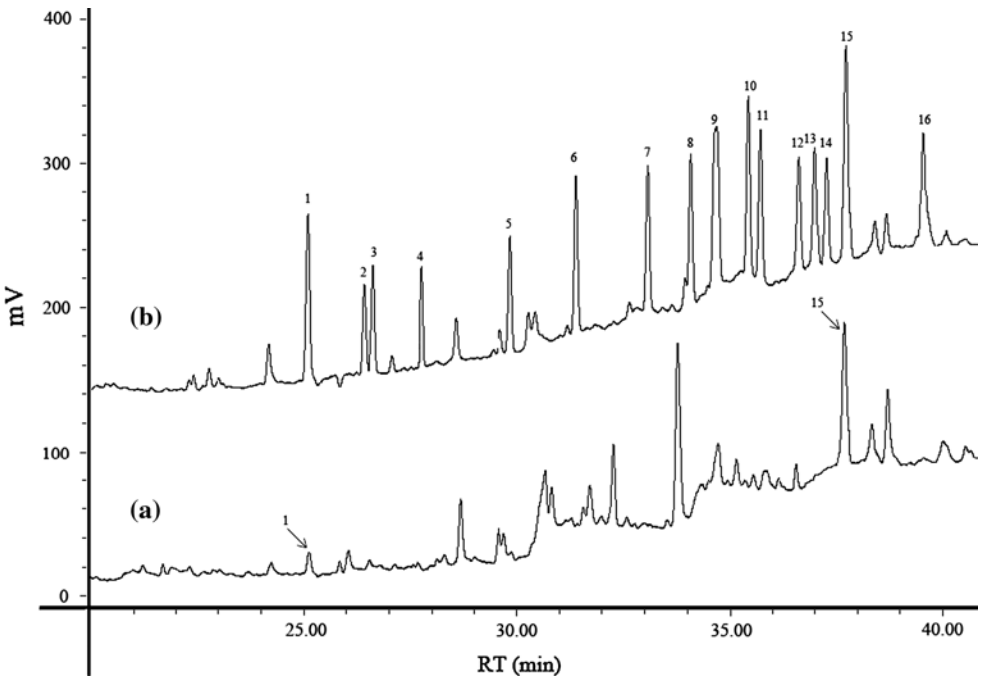

Fig. 4 Chromatogram of grape sample before (**a**) and after (**b**) spiking with 10 ng g^{-1} OCPs

for the OCPs were in the range between 75.5 and 115.3 %, indicating a good performance of the presented method for determination of the OCPs in fruit samples. Figure 4 shows typical chromatograms of the extracted OCPs from grape sample before and after spiking with 10 ng g^{-1} of OCPs.

Conclusions

The results of the present study revealed that extraction and determination of OCPs in water and fruit samples can be performed using HLLE–GC–ECD method. The sedimented chloroform phase obtained in the present work is a simple matrix in comparison with the cloud point or pH-dependent HLLE systems. Comparison of this method with other methods demonstrated that HLLE method provides high recovery and preconcentration factor at a very short time. Further, it is simple, inexpensive, highly sensitive with low limit of detection, and can be successfully applied to separation, preconcentration, and determination of not only OCPs but also other noxious materials from different real samples.

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