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EFFERVESCENCE-ASSISTED DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR EXTRACTION AND PRECONCENTRATION OF ORGANOCHLORINE PESTICIDES IN WATER SAMPLES

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ABSTRACT. In this paper, effervescence-assisted dispersive liquid-liquid microextraction method has been developed for the extraction and preconcentration of organochlorine pesticides in water samples before their determination by gas chromatography-mass spectrometry. The method involves *in-situ* generation of CO_2 bubbles to induce dispersion of the extraction solvent in the aqueous sample. Different parameters affecting the extraction efficiency of the method including the type and concentration of the effervescent agents as well as the type and volume of extraction solvent were optimized. Under optimum conditions, matrix matched calibration curves were constructed at eight concentrations ranging from 0.6–4.0 ng/mL showed good linearity with coefficient of determinations of ≥ 0.9961. The limits of detections and quantifications ranged from 0.2–0.4 and 0.6–1.0 ng/mL, respectively. The intra- and inter-day precisions studied at two concentration levels had below 5% relative standard deviation values. Similarly, recoveries investigated at two concentration levels ranged from 80.7–117.4%. The findings demonstrated that proposed method is simple, rapid, and efficient to be used as alternative method for analysis of organochlorine pesticides from environmental water and other similar matrices.

KEY WORDS: Effervescence agents, CO_2 bubbles, Organochlorine pesticides, Water samples, gas chromatography-mass spectroscopy

INTRODUCTION

Organochlorine pesticides (OCPs) are synthetic organic pesticides that have been used in agriculture to control insect pests for wide variety of crops, and in the health sector to control diseases like malaria [1]. These pesticides are toxic and resistant to physical, chemical, and biological degradations. After applications, their residues can persist in the environment for a long time [2] and be able to bioaccumulate and biomagnify through the food chain [3]. These days, the application of OCPs is banned worldwide due to their toxicity and persistence in the environment [4]. However, due to their low cost, availability, and effectiveness against numerous pests, OCPs are still used in developing countries to control pests from crops such as vegetables [5, 6] and fruits [7]. During and/or after their applications, these pesticides can enter the nearby aquatic environments through precipitation, drift, infiltration, or soil erosion (water runoff). The residue of these pesticides is expected to exist at trace and/or ultra-trace levels in environmental waters. Thus, sensitive and selective analytical sample preparation methods are required for their analysis [8]. These methods involve the use of appropriate sample preparation procedures before their quantitative determination by analytical techniques.

Sample preparation involves extraction/isolation, preconcentration, and/or clean-up steps [9]. Traditional sample preparation procedures such as liquid–liquid extraction (LLE) [10] and solid phase extraction (SPE) [11] have been widely used for the extraction of OCPs from various matrices. However, these methods have inherent drawbacks, such as being time-consuming, labor-intensive, use large organic solvent volumes, and poor selectivity. In the last few decades, several miniaturized sample preparation methods that either reduce or eliminate the use of toxic organic solvents have been reported. These methods include solid phase microextraction (SPME)

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[12], single drop microextraction (SDME) [13, 14], hollow fiber–liquid phase microextraction (HF-LPME) [15, 16], and dispersive liquid–liquid microextraction (DLLME) [17]. Among these methods, DLLME has been widely used for extraction and/or preconcentration of various organic and inorganic chemicals from different matrices due to its simplicity of operation, speed, versatility, low organic solvent, and sample volume consumption, as well as high recovery and enrichment factor [18-21].

DLLME method was first introduced by Rezaee and coworkers in 2006 [22]. The original DLLME method involves the dispersion of a water-immiscible organic solvent (extraction solvent) into the aqueous solution using a water-miscible disperser solvent [23, 24]. During this process, the fine droplets of the extraction solvent are homogeneously distributed throughout the sample solution; and thus remarkably enhance the rate of the partitioning of analytes between phases. However, its environmental greenness has become debatable due to the use of additional organic solvent as a dispersant. Besides, a disperser solvent can also enhance the solubility of target analytes and the extraction solvent into the aqueous phase, resulting in reduced extraction efficiency of the method. Thus, various DLLME modalities that disperse the extraction solvent by other auxiliary techniques such as vortex mixer, sonication, mechanical shaker, and air purging have been reported. Some of these methods are vortex-assisted DLLME [25, 26], ultrasound-assisted DLLME [27], up-and-down shaker-assisted DLLME [28, 29], salt-assisted LLME [30], and air-assisted LLME [31, 32]. Nevertheless, some of these modified methods require special apparatus and long extraction time. Moreover, in ultrasound-assisted DLLME, the sonication process may cause analyte decomposition. Recently, another novel effervescence-assisted DLLME (EA-DLLME) was reported in 2014 by Lasarte-aragonés and coworkers [33]. In this method, the extraction solvent is dispersed by CO_2 bubbles, *in-situ* generated from an effervescent reaction between the CO_2 source and the proton donor [33–42]. EA-DLLME procedure can be performed either by first dissolving CO_2 source to an aqueous sample, followed by rapid injection of mixture of a proton donor and an extraction solvent [33, 34] or by placing a tablet or powder containing CO_2 source and proton donor in a reaction tube to disperse the extraction solvent into the aqueous sample [35-42]. The method is easy, quick, effective, and environmentally friendly.

Recently, we reported an effervescent-powder assisted floating organic solvent-based DLLME for analysis OCPs in environmental water by GC-MS [41]. The findings showed that the proposed method is efficient for analysis of the OCPs in environmental water samples and related matrices. The obtained findings, encouraged the researchers to develop additional alternative EA-DLLME procedure that use denser organic or other solvents as an extractant.

Therefore, the primary goal of this study was to develop EA-DLLME procedure that use higher density organic solvent as an extractant for selective extraction and preconcentration of OCPs from environmental water samples before their separation and quantitative analysis by GC-MS. In this procedure, an appropriate amount of CO_2 source was initially dissolved in aqueous samples and then, a mixture of extractant and proton donor were injected. Various parameters affecting the extraction efficiency were studied and the optimum conditions were established. The performances of the method were evaluated by applying proposed method to different environmental water samples.

EXPERIMENTAL

Chemicals and standards

Analytical grade OCPs standards namely: benzene hexachloride (BHC) (α-BHC, 99.5%, β-BHC, 99.5%, and δ-BHC, 99.5%), eldrin (98.8%), gamma-Chlordane (γ-Chlor) (98.8%), *p,p'*-DDE (99.99%), endrin (99.3%), *p,p'*-DDT (98.9%), endosulfan sulphate (ESS) (98.8%), dieldrin (97.9%), methoxychlor (MC) (97.7%), and dibutyl chlorednate (DBC) (99.5%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Analytical grade solvents including dichloromethane, chloroform, carbon tetrachloride, and hexane were obtained from Loba Chemie Pvt. Ltd (Mumbai, India). The analytical reagents including glacial acetic acid and formic acid were purchased from Merck (Darmstadt, Germany) and Finekem laboratories Pvt. Ltd (Aurangabad, India), respectively. Sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$) and potassium carbonate (K_2CO_3) were obtained from Fisher Scientific Limited (UK).

Individual stock standard solutions, 400 mg/L of DDE, DDT, gamma chlordane, dieldrin, endrin, ESS, and MC; 1000 mg/L dibutyl chlordane (DBC), β-BHC, δ-BHC, and α-BHC, as well as 800 mg/L aldrin were prepared in hexane. A mixed intermediate standard solution containing 20 mg L^{-1} of each OCP was prepared in hexane from the stock solutions. All prepared standard solutions were stored at 4 °C in a refrigerator unless they were used for analysis. Working standard solutions were daily prepared by diluting the mixed intermediate standard solution in hexane.

Instrumentation

An Agilent 8890A gas chromatography (GC) with a 5977B mass spectrometry detector (MSD) (Agilent Technologies, USA) was used for analyzing OCPs. An HP-5MS fused-silica capillary column (30 m 0.25 mm i.d. x 0.25 µm film thickness) coated with a 5% diphenyl-95% dimethylsiloxane (Agilent Technologies) was used for separating OCPs. A 5-mL medical syringe with B. Braun Sterican needle 21 G x 4¾ (0.80 x 122 mm BL/LB) obtained from B. Braun Melsungen AG (Melsungen, Germany) and 15 mL falcon centrifuge tubes were used during sample preparation.

EA-DLLME procedure

Deionized water, 10 mL, was taken into a 15-mL falcon tube and then spiked with appropriate concentration of target OCPs standard solution and kept for 20 min for equilibration. Afterward, 200 µL of 2.25 mol/L K_2CO_3 was added and thoroughly mixed by manual shaking for a few seconds. Subsequently, 150 µL extraction solvent (chloroform) and 400 µL of 3.5 mol/L formic acid were slowly injected using a syringe, placing the needle at the bottom of the falcon tube. The effervescent reaction took place in less than 3 s from the bottom to the top of the tube, and thus, the extraction solvent was homogeneously dispersed into the aqueous phase. When the effervescence reaction was completed, the content was centrifuged for 1 min at 4000 rpm. Finally, the lower organic phase was withdrawn and transferred to autosampler vial for the GC-MS analysis.

GC-MS operating conditions

High purity helium, 99.9999%, was used as the carrier gas at a flow rate of 1 mL/min. The sample, 1 µL, was injected in split less mode. The injection port temperature was adjusted to 280 °C. The GC oven temperature programme was: initial temperature 100 °C; ramped at 15 °C/min to 200 °C held (for 5 min); ramped at 4 °C/min to 250 °C (held for 2 min); and finally ramped at 10 °C/min to 270 °C (held for 10 min). The temperatures of GC-MSD transfer line, MSD ion source, and quadrupole were 280, 230, and 150 °C, respectively. The MSD was operated in electron ionization mode with ionization energy of 70 eV by scanning from m/z 45 to 500 at 150 s/scan; and 3 min solvent delay time. Determination of OCPs was performed in the selected ion monitoring (SIM) mode using one quantitative and two qualifier ions. The lists of OCPs; molar mass, the quantitative ion, qualifier ions, and retention time of the studied pesticides are presented in Table 1.

Table 1. Lists of OCPs molar mass, quantitative ion, qualifier ions and retention time the ions.

Analytes	Molar mass (g/mol)	Quantitative ion (m/z)	Qualifier ion (m/z)	Retention time (min)
α-BHC	290.83	219	189, 109	7.8
β-BHC	290.83	219	189, 109	8.5
δ-BHC	290.83	219	189, 109	10.08
Aldrin	364.9	263	66, 293	12.44
γ-Chlor	409.8	272	65,373	15.032
DDE	318.02	246	176, 318	17.38
Endrin	380.9	281	263,345	18.75
DDT	354.49	212	165, 235	19.25
ESS	422.9	272	229, 387	21.8
Dieldrin	380.9	280	249, 379	23.28
MC	345.6	240	227, 274	24.88
DBC	499	237	99, 388	25.25

Calculation of enrichment factor

The enrichment factor (EF) was determined from the ratio of the OCPs concentration in the lower organic phase ($C_{organic\ phase}$) to the initial spiked concentration of OCPs (C_{spiked}) in the aqueous sample:

$$\mathrm{EF} = {C_{organic\ phase}}\Big/{C_{spiked}}$$

RESULTS AND DISCUSSION

Optimization of EA-DLLME experimental conditions

Different parameters influencing the extraction efficiency of the proposed EA-DLLME were investigated using one-variable-at-a-time. Deionized water (10 mL) spiked with known concentration of each OCP was used during optimization studies. All experiments were performed in triplicate (n = 3).

Selection of effervescent agents

In the EA-DLLME procedure, the choice of appropriate effervescent agents, both a CO_2 source and a proton donor, plays an important role in enhancing the dispersion of the extraction solvent and the transfer of the analytes. The amount of CO_2 bubbles, *in-situ* generated via effervescence reaction depends on the type and composition of the effervescent agents [37]. In this study, salts such as Na_2CO_3, K_2CO_3, and $NaHCO_3$ were investigated as CO_2 sources and chloroform was used as the extraction solvent. To choose the CO_2 source, each salt was separately combined with formic acid (the proton donor), depending on their stoichiometry (1:2 mole ratios) in the effervescence reaction. The results showed that K_2CO_3 provided the best extraction efficiency than the other two salts (Figure 1a). The observed variations among the studied CO_2 sources might be due to their differences in effervescence time and dispersion efficiency [38]. Thus, K_2CO_3 was chosen as CO_2 source in further study.

Likewise, acetic acid and formic acid were studied as the proton donor in the presence of K_2CO_3 as a CO_2 source. The obtained results (Figure 1b) demonstrated that formic acid provided better extraction recoveries than acetic acid and thus it was selected in further studies.

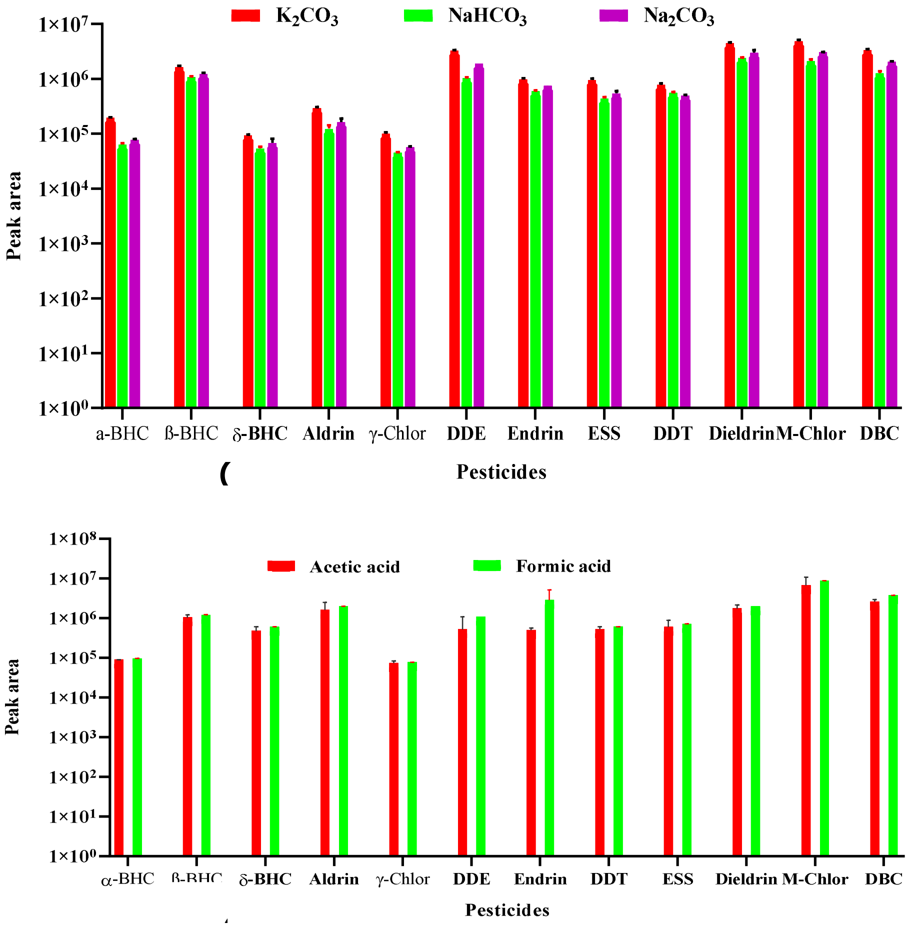

Figure 1. Effects of the types of (a) CO_2 source and (b) proton donor on the extraction efficiency of the method.

Effect of K_2CO_3 concentration

The concentration of CO_2 source is another important factor affecting extent of the effervescence reaction and the dispersion of extraction solvent [39]. The effect of K_2CO_3 concentration was investigated from 0.75–2.75 mol/L. During this study chloroform (150 µL) was used as extraction solvent. For each concentration level, 200 µL was combined with 400 µL of 3.5 mol/L formic acid. The extraction efficiency of the method increased with the concentration of CO_2 source up to 2.25 mol/L and then decreased at higher concentrations (Figure 2). When the concentration of K_2CO_3 raises the effervescence reaction time, the amount of CO_2 bubbles generated increases, which also enhances the dispersion of the extraction solvent and the transfer of the analytes. However, the use of higher concentrations of K_2CO_3 may facilitate solubility of the extraction solvent and/or the analytes into the aqueous solutions due to the extended reaction time. Thus, 2.25 mol/L was chosen for further experimental studies.

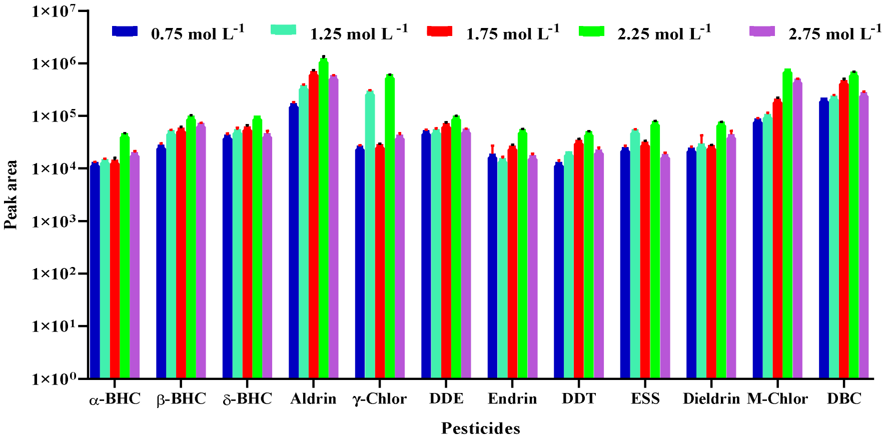

Figure 2. Effect of concentration of K_2CO_3 on the extraction efficiency of the method.

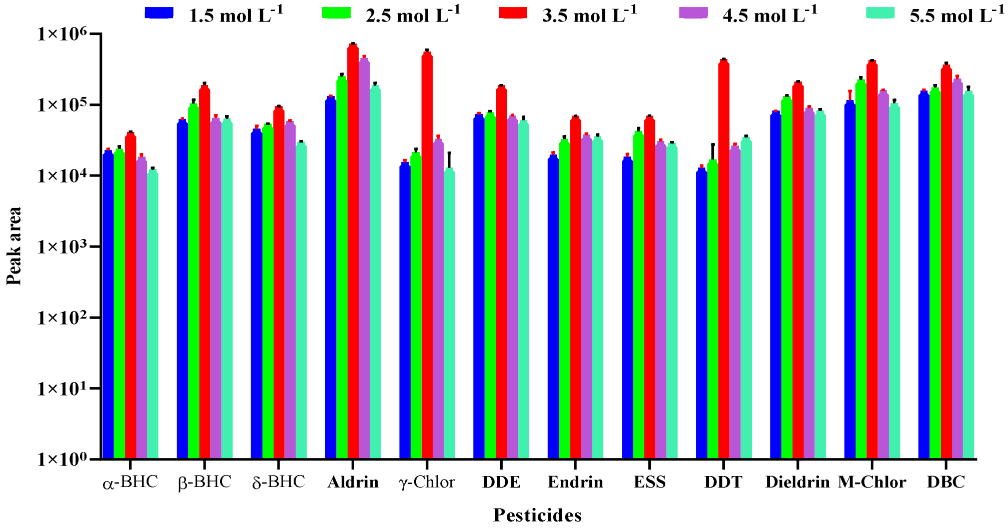

Figure 3. Effect of concentration of formic acid on the extraction efficiency of the method.

Effect of formic acid concentration

To evaluate the effect of formic acid concentration on the extraction efficiency of OCPs, different concentration levels were investigated in the range of 1.5–5.5 mol/L. At each concentration level, 400 µL was combined with 200 µL of 2.25 mol/L K_2CO_3. Figure 3, shows the effects of the concentration of formic acid on the extraction efficiency of the method for the target OCPs. The obtained results indicated that the extraction efficiency was increased with the concentration of the acid up to 3.5 mol/L and then the efficiency declined upon further increase the acid concentrations. Therefore, 400 µL of 3.5 mol/L of formic acid was used in subsequent experiments.

Extraction solvent selection

The extraction performance of an EA-DLLME method is greatly influenced by the type of extraction solvent. The selected extraction solvent should meet the criteria including low water solubility, higher density than water, high affinity for the target analytes, and compatibility with the method of analysis, GC-MS [40]. Accordingly, in this study, three solvents: chloroform, dichloromethane, and tetrachloromethane were investigated using 5 mol/L formic acid (400 µL) and 2.25 mol/L K_2CO_3 (200 µL) as effervescent agents. As can be seen from Figure 4, the three solvents showed nearly similar extraction efficiencies for all analyses. However, relatively the highest peak areas were obtained for the target OCPs when chloroform was used, and thus, chloroform was selected for further experiments.

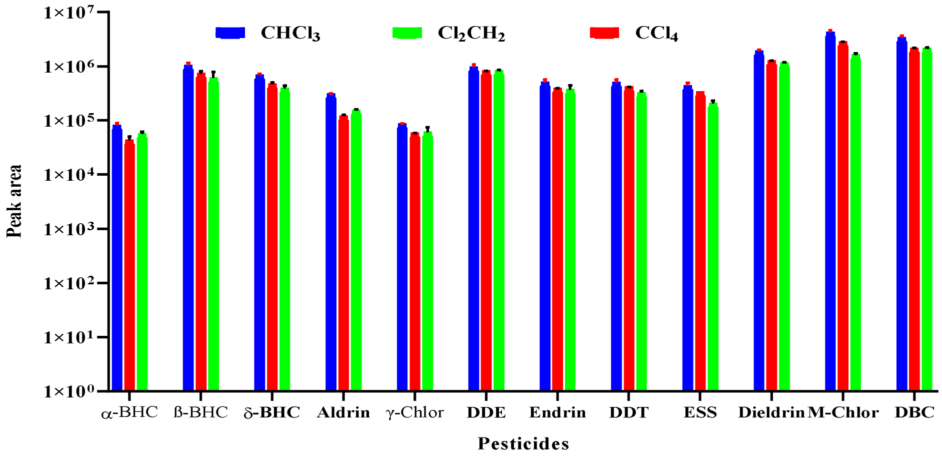

Figure 4. Effect of extraction solvent type on the extraction efficiency of the method.

Effect of volume of extraction solvent

Another core aspect that influences extraction efficiency of EA–DLLME method is the volume of the extraction solvent [41]. Different volumes of chloroform in the range of 90–210 µL were evaluated at 30 µL interval to select the optimum extraction solvent volume. The obtained results are presented in Figure 5. The findings demonstrated that the peak areas of the OCPs increased with increasing the extraction solvent volume from 120 to 150 µL, then gradually declined at higher extraction solvent volumes which might be due to the dilution effect [42]. When lower volumes, below 150 µL of chloroform was used, the volume of the organic phase obtained after extraction was very small and difficult to collect for the subsequent analysis. Therefore, 150 µL of chloroform was chosen as the optimum volume for further studies.

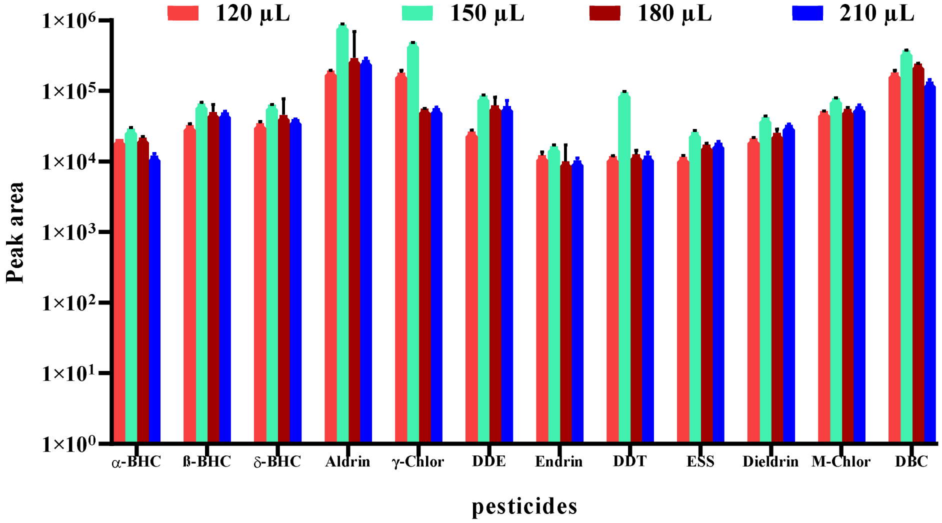

Figure 5. Effect extraction solvent volume on the extraction efficiency of the method.

Analytical performance characteristics

Under the optimum conditions, the analytical performance characteristics of the method were evaluated in terms of linear dynamic range (LDR), coefficient of determination (R^2), limits of detection and quantitation (LOD and LOQ), intra- and inter-day precisions, and enrichment factor (EF). Table 2 shows the analytical performance characteristics of the method. Linearity of the proposed method was evaluated by constructing matrix matched calibration curves at eight concentrations ranging from 0.6–4.0 ng/mL. The R^2 values of the curves were varied from 0.9961–0.9992, indicating acceptable linearity of the calibration curves in the studied concentrations range. The LOD and LOQ which were determined as 3 and 10 times signal-to-noise ratio were in the ranges of 0.2–0.4 and 0.6–1.0 ng/mL, respectively. The inter- and intra-day precisions expressed as relative standard deviations (RSD) were evaluated at two concentration levels: Level 1: 1.5 ng/mL, and Level 2: 3.0 ng/mL. For intra-day precision study, three replicate samples extracted for each concentration level and then, each extract was injected in duplicates on the same day (n = 6). Inter-day precision was studied for four consecutive days, by extracting a sample per day for each concentration level and injecting the extract in triplicates (n = 12). The obtained %RSD values at Level 1 and Level 2 were: 0.7–4.4, and 0.6–1.5 (intra-day) as well as 0.8–4.7 and 0.5–3.2 (inter-day), respectively. The EF of the method were ranged from 13.1–160.2.

Analysis of real samples

Three water samples namely ground, river, and tap were used to evaluate applicability of the proposed EA-DLME method for extraction and preconcentration of OCPs followed by their determination using GC-MS technique. Groundwater sample was collected from Kochi area, Jimma Town, Ethiopia. River water sample was taken from Awetu River, a river that crosses the town. Tap water was collected from Jimma University Analytical Chemistry Lab after 10 min flowing. Water samples were filtered using Whatman filter paper No. 1 before spiking with the

Table 2. Analytical performance characteristics of the proposed EA–DLLME.

Analyte	LDR (ng/mL)	R^2	LOD (ng/mL)	LOQ (ng/mL)	%RSD (Intra-day)		% RSD (Inter day)		EF
					Level 1	Level 2	Level 1	Level 2	
α-BHC	0.8–4.0	0.9985	0.3	0.8	3.0	1.4	4.7	1.8	52.9
β-BHC	0.7–4.0	0.9985	0.2	0.7	3.3	1.3	4.5	1.2	13.1
δ-BHC	0.9–4.0	0.9974	0.3	0.9	0.7	0.6	1.2	0.9	99.7
Aldrin	0.9–4.0	0.9970	0.3	0.9	1.7	1.0	1.5	1.4	14.4
γ-chlor	0.6–4.0	0.9992	0.2	0.6	0.9	0.6	2.4	1.5	111.2
DDE	0.9–4.0	0.9984	0.3	0.9	2.3	0.8	2.2	1.6	73.3
Endrin	1.0–4.0	0.9965	0.4	1.0	4.4	0.8	4.0	3.2	34.4
DDT	0.8–4.0	0.9964	0.3	0.8	1.5	1.4	1.2	1.0	36.6
ESS	0.9–4.0	0.9974	0.3	0.9	1.8	1.5	1.3	1.0	160.2
Dieldrin	1.0–4.0	0.9961	0.4	1.0	0.8	0.6	1.9	1.7	34.8
M-chlor	0.8–4.0	0.9974	0.3	0.8	1.3	0.7	1.6	0.9	37.4
DBC	0.7–4.0	0.9989	0.3	0.7	0.8	0.7	0.8	0.5	65.9

Level 1: 1.5 ng/mL; and Level 2: 3 ng/mL.

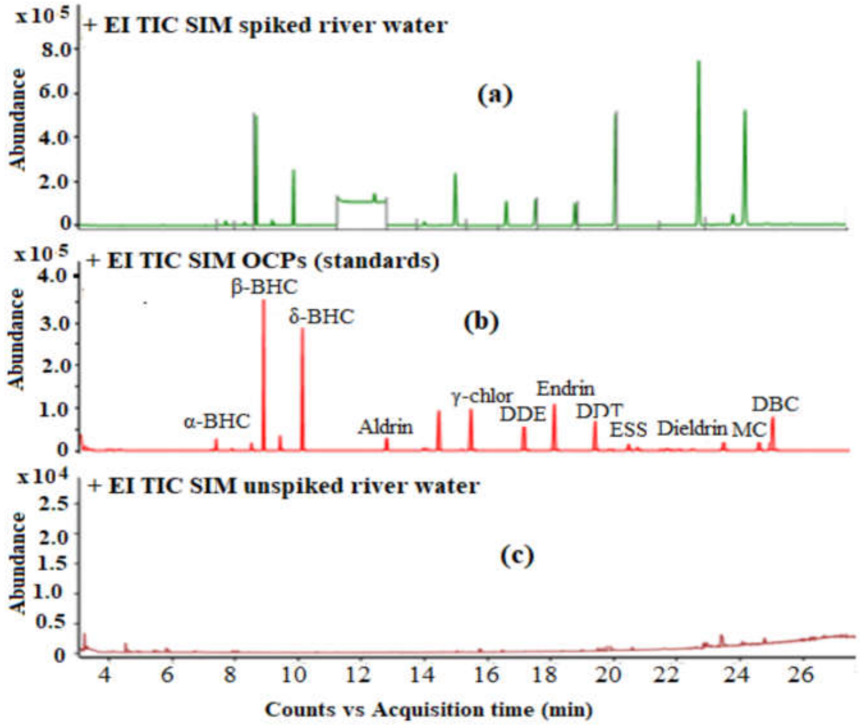

Figure 1. GC-MS chromatograms of (a) spiked river water, (b) standards of OCPs, and (c) unspiked water sample.

target OCPs and employing the proposed EA-DLLME method for extraction. The target OCPs were not detected in the three water samples. To investigate matrix effects, relative recoveries (%RR) were studied by spiking the water samples with the OCPs at two concentration levels as previously used in precision studies. The ratio of peak areas obtained in real and de-ionized water samples spiked at the same concentrations level was used to calculate %RR. The obtained %RR were in the range of 80.7–117.4%, with RSD values of less than 6 for all samples (Table 3), indicating the different water samples have no significant matrix effects on the analysis of the target OCPs by the proposed method. Figure 6 shows representative GC-MS chromatograms of (a) spiked river water, (b) standards of OCPs, and (c) blank (unspiked) water sample.

Table 3. Relative recoveries, % and RSD% of the target analytes in the samples spiked at two concentration levels (n = 6).

Analyte	Ground water		River water		Tap water	
	Level 1	Level 2	Level 1	Level 2	Level 1	Level 3
α-BHC	91.8 ± 1.5	97.9 ± 2.7	99.3 ± 1.9	85.8 ± 0.7	99.5 ± 2.8	105.5 ± 4.4
β-BHC	100.2 ± 0.9	117.4 ± 0.8	101.7 ± 0.1	96.5 ± 0.1	97.2 ± 1.8	96.6 ± 1.2
δ-BHC	109.4 ± 5.1	82.9 ± 0.7	115.1 ± 2.9	96.9 ± 2.5	106.3 ± 2.0	106.3 ± 3.7
Aldrin	94.4 ± 2.1	104.3 ± 4.7	91.5 ± 2.2	91.5 ± 5.7	105.4 ± 3.0	108.1 ± 0.6
γ-Chlor	93.8 ± 0.6	92.6 ± 0.1	90.6 ± 3.7	98.3 ± 0.1	107.8 ± 0.6	97.4 ± 1.1
DDE	108.7 ± 0.7	112.9 ± 2.0	106.2 ± 0.2	97.9 ± 1.1	100.9 ± 0.7	103.9 ± 0.1
Endrin	106.4 ± 1.7	108.6 ± 0.6	97.7 ± 2.0	99.3 ± 1.4	108.9 ± 0.8	96.2 ± 0.8
DDT	104.2 ± 0.7	99.4 ± 0.5	96.5 ± 1.4	87.9 ± 3.8	100.9 ± 1.3	95.1 ± 0.7
ESS	80.7 ± 1.5	83.3 ± 1.4	82.8 ± 5.7	90.5 ± 1.3	105.6 ± 2.3	108.4 ± 2.6
Dieldrin	92.3 ± 1.4	98.4 ± 1.7	97.9 ± 0.5	98.9 ± 1.1	102.3 ± 0.6	105.3 ± 1.4
M-Chlor	107.1 ± 3.7	98.1 ± 5.4	109.9 ± 1.1	110.5 ± 2.9	105.6 ± 2.3	80.9 ± 0.7
DBC	103.1 ± 1.0	106.3 ± 0.1	102.6 ± 0.4	101.9 ± 3.1	108.2 ± 0.9	102.5 ± 0.1

Table 4. Comparison of various methods for analysis of organochlorine pesticides.

Method	Sample	Sample size (mL)	Extraction time (min)	LDR	LOD (ng/mL)	%RSD	Recovery, %	Ref.
HLLE-GC-ECD	Water and fruit juice	5	5	0.01–100	0.001–0.03	4.9–8.6	75.5-115.3	[7]
SDME-GC-ECD	Tea brew	5	25	0.6–10	0.01–0.025	1.0–24	92.0–116.0	[13]
DLLME-GC-MS	Water	10	–	0.5–16	0.001–0.025	5–15	70.0–120.0	[17]
EPA-FOS-DLLME	Water	10	-	0.4–2.8	0.03–0.24	0.3–5.5	76 -116	[41]
LDS-DLLME-GC-ECD	Snow water	20	3	0.08–100	0.02–0.11	1.6–14.8	71.1–97.1	[43]
GDME-GC-ECD	Milk	20	30	2.5–40	3.70–4.80	0.8–9.3	71.0–99.0	[44]
M-SPE-GC-MS/MS	Water	5	20	1.0–200	0.07–1.03	1.0–8.5	74.9–116.3	[45]
EA-DLLME-GC-MS	Water	10	< 1	0.6–4.0	0.20–0.40	0.6–4.9	75.4–117.4	This study

DLLME: Low density solvent based dispersive liquid-liquid microextraction; EPA-FOS-DLLME: effervescent powder-assisted floating organic solvent-based DLLME; GC-ECD: gas chromatography electron captured detector; HLLE: homogenous liquid–liquid microextraction; SDME: single drop microextraction; LDS- GDME: gas diffusion microextraction; M-SPE-GC-MS/MS: magnetic–solid phase extraction gas chromatography–tandem triple quadrupole mass spectrometry.

Comparison of the developed method with other approaches

The performance of the proposed EA-DLLME method has been compared with other reported methods used for analyses of OCPs in various matrices. The methods were compared in terms of their analytical performance characteristics such as LDR, LOD, RSD, and %RR. As can be seen in Table 4, the proposed method showed wide LDR, low RSD (better precision), better and/or comparable LOD, and %RR to other reported microextraction method. Furthermore, the proposed EA-DLLME is faster or has a short extraction time than other microextraction techniques. Unlike conventional DLLME, it also does not use organic solvent as a disperser. The proposed EA-DLLME method also does not require auxiliary devices such as vortex agitator, and ultrasound sonicator to enhance dispersion of the extraction solvent.

CONCLUSIONS

In this study, EA-DLLME has been employed for the extraction and preconcentration of 12 OCPs from aqueous samples before their separation and quantitative determination by GC-MS. K_2CO_3 and formic acid were used as effervescence agents; for in-situ generation of CO_2 bubbles for dispersing the extraction solvent, chloroform, in the aqueous solution. Unlike other conventional and other modified DLLME procedures, the method does not use organic solvent as disperser solvent and auxiliary devices such as vortex, ultrasound sonicator, etc. It also showed satisfactory analytical performance characteristics such as LDR, LOD, intra-, and inter-day precisions, EF, and %RR for analysis of the target OCPs in water samples. In addition, the method is simple, fast, and consumes less extraction solvent. Therefore, the proposed EA-DLLME method is a promising extraction and preconcentration method to be employed in monitoring of the residual OCPs and related pesticides from different water samples and other related matrices.

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