



## Research article

# Effervescent powder-assisted floating organic solvent-based dispersive liquid-liquid microextraction for determination of organochlorine pesticides in water by GC–MS

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## ABSTRACT

An effervescent powder-assisted floating organic solvent-based dispersive liquid-liquid microextraction was introduced for determination of 13 organochlorine pesticides in water samples. In this method, a less toxic low-density organic solvent was used as extraction solvent. The extraction solvent was dispersed in to the aqueous sample via CO<sub>2</sub> bubbles, *in-situ* generated up on addition of water to a falcon tube containing the mixture of effervescent powder precursors as well as the extraction solvent. Various experimental parameters such as effervescent and its weight fractions, extraction solvent type and its volume, the total mass of effervescent precursors, and the effect of salt were investigated and the optimal conditions were established. Under the optimum conditions, the proposed method exhibited good linearity for all target pesticides with the coefficient of determinations varying from 0.9981 to 0.9997. The limits of detection and quantification were within the range of 0.03–0.24 and 0.26–0.75 µg/L, respectively. The intra- and inter-day precisions which were expressed in terms of the relative standard deviation ranged from 0.33 to 4.47 and 0.51–5.52%, respectively. The enrichment factors and recoveries ranged from 24 to 293 and 76–116%, respectively. The proposed method could be used simple, cheap, fast, and environmentally friendly alternative for analysis of organochlorine pesticides from environmental water and other similar matrices.

## 1. Introduction

Each year, approximately three billion kilograms of pesticides are utilized around the world. In any case, as it were 1–5% of the whole pesticides are successfully utilized to control pests or target organisms [1,2]. After use, most of these pesticides are left as residues or enter into non-target organisms. Pesticides residues can be transported to the different environmental compartments through water runoff, drift, leaching, and accidental/neglected spilling [3] and, thus, can pollute air, soil, and water bodies such as drinking water, surface, and well water [4–7]. Pollution of an aquatic environment can harm human health and aquatic life.

From various type of pesticides, organochlorine pesticides (OCPs) are highly toxic and resistant to biological and chemical degradation. They can cause acute health problems: headaches, skin irritation, breathing difficulties, and nausea [4], and chronic diseases such as cancer [8,9], birth defects [10] and autoimmune disorders [11]. However, due to their toxicity, several OCPs were

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banned from use worldwide. Nevertheless, several developing countries including Ethiopia have been used these pesticides to control malaria [12]. Thus, monitoring of residues OCPs in various environmental samples is important and a global concern.

Analysis of pesticide residues in real samples requires a sample preparation step. Traditional sample preparation methods: liquid-liquid extraction [13], and solid-phase extraction [14] are widely used for extraction and pre-concentration of pesticide residues from water and other matrices. However, they are time-consuming, labor-intensive, require large sample-to-solvent ratios, and use toxic organic solvents [15]. To reduce these drawbacks, various miniaturized sample preparation methods including liquid phase microextraction [16] and solid phase microextraction [17] were proposed in different modalities.

Among various LPME techniques, dispersive liquid-liquid microextraction (DLLME) is widely used for the extraction and pre-concentration of pesticides residues from water and other matrices [15,18]. However, the method mainly uses high volume of disperser and higher density toxic organic solvents or ionic liquids as extraction solvents [19]. Scholars are still working on modification of the method, to either eliminate use of the disperser and/or to replace the extraction solvent with less toxic organic solvents.

Recently, an effervescent-assisted DLLME method was reported as one of the best alternative modalities of the DLLME. The method uses CO<sub>2</sub> bubbles to disperse the extraction solvent in the sample. CO<sub>2</sub> bubbles are *in-situ* generated from effervescent reaction between an effervescent agent and a proton donor [20,21]. In this reaction carbonates or bicarbonates of alkali or alkaline earth metals are used as effervescent agents, and organic acids such as citric acid (CA), oxalic acid (OA), tartaric acid (TA), or formic acid (FA), or inorganic acids/salts such as NaH<sub>2</sub>PO<sub>4</sub>, HCl or H<sub>2</sub>SO<sub>4</sub> are used as proton donors [22]. The method has been used for extraction and/or pre-concentration of different classes of pesticides including pyrethroid and carbamates from edible oil [23]; methadone in water and biological samples [24]; fungicides from different fruit and apple juices [25,26]; triazine herbicides and fungicides from water and grape juices [27,28]; benzoylureas [29], and pyrethroid insecticides in water [30]. However, to date there is no report on the use of an effervescent powder-assisted floating organic solvent-based DLLME (EPA-FOS-DLLME) procedure for determination of OCPs from environmental water samples or other matrices.

Therefore, in this study EPA-FOS-DLLME has been proposed for extraction and pre-concentration of 13 OCPs in water samples prior to their determinations by GC-MSD. Different parameters influencing performance of the method were studied and the optimal conditions were established. The analytical merits of the method were validated following the standard procedures [31] and the obtained findings were compared with other recently reported methods. Applicability of the method was evaluated by determining residues of the target analytes in Tap, River and Well water samples.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Analytical standards of OCPs including benzene hexachlorides (BHC) including  $\alpha$ -BHC (99.5%),  $\beta$ -BHC(99.5%), and  $\delta$ -BHC (99.5%); dichlorodiphenyltrichloroethane, DDT (98.9%); Dichlorodiphenyldichloroethylene, DDE (99.9%); chlorinated cyclodienes including endosulphan sulfate, ESS (98.8%); endrin (99.3%);  $\gamma$ -chlordane (98.8%); heptachlor epoxide, HCE (98.8%); aldrin ( $\geq$ 98.8%); dieldrin (97.9%); methoxychlor, MC (97.7%); and dibtylchlorindate, DBC (99.5%) were obtained from Sigma Aldrich (St. Louis, MO, USA).

The analytical reagents of sodium bicarbonate (NaHCO<sub>3</sub>), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) were obtained from Fisher Scientific (UK). Monohydrate citric acid, tartaric acid, oxalic acid, and 1-octanol were supplied by Blulux® laboratories (Shanghai, China), Kemie labs (Mumbai, India), and Lianyungang (Jiangsu, China), respectively. GC grade organic solvents including toluene was purchased from Nice Chemicals Pvt. Ltd, (Ernakulam, India), cyclohexanol and hexane were purchased from Loba Chemie Pvt. Ltd (Mumbai, India). Deionized water was used as a sample during the method optimization studies. Whatman® filter paper (grade 1) purchased from Whatman International Ltd (Maidstone, England) was used for filtration of water samples.

Individual standard stock solutions (1000 mg/L) of  $\alpha$ -BHC,  $\beta$ -BHC,  $\delta$ -BHC, and DBC; 400 mg/L of DDT, DDE, dieldrin, ESS, HCE,  $\gamma$ -chlordane, MC, and endrin as well as 800 mg/L aldrin were prepared in hexane. A mixed standard solution (20 mg/L) was prepared by diluting the stock solutions in hexane. The prepared solutions were stored below 4 °C when not used for analysis.

Appropriate molar ratios of the CO<sub>2</sub> sources: K<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> and the proton donors: CA, OA, and TA were mixed together. Then, the mixtures were manually ground using mortar and pestle to obtain homogenized and fine powders.

### 2.2. Instrumentation

An Agilent 8890 GC coupled with an Agilent 5977B single quadruple MSD and Agilent G4513A autosampler (Agilent technologies, USA) was used for analysis of OCPs. An HP-5MS capillary column (30 m, 0.25 mm i. d, 0.25  $\mu$ m film thickness) coated with 5% diphenyl/95% dimethylsiloxane obtained from Agilent technologies was used for the analytes separation. 15-mL falcon centrifuge tubes and medical syringe were used during sample preparation.

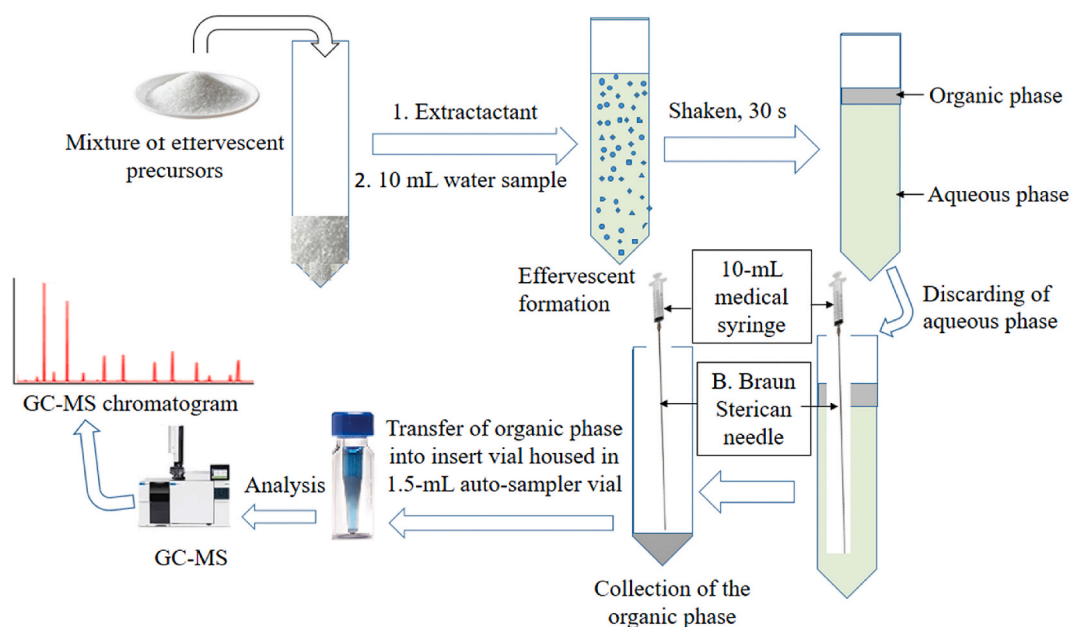
### 2.3. GC-MSD operating conditions

High purity (99.999%) helium was used as carrier gas at 1 mL/min flow rate. The sample (1  $\mu$ L) was injected in the spitless mode. The GC 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 4 min; and finally ramped at 10 °C/min to 270 °C, held for 10 min; and the injector port temperature was 280 °C. The MSD was operated in electron ionization mode with an ionization energy of 70 eV, GC-MSD transfer line temperatures 250 °C; ion

**Table 1**

Molar mass, quantitative ion, qualifier ions and retention time's ions selected for the analysis of OCPs using GC-MS analysis.

Analytes	MW (g/mol)	RT (min)	Quantitative ion ( $m/z$ )	Qualifier ions ( $m/z$ )
$\alpha$ -BHC	290.83	7.87	219	189, 109
$\beta$ -BHC	290.83	9.52	219	189, 109
$\delta$ -BHC	290.83	10.08	219	189, 109
Aldrin	364.9	11.78	263	66, 293
HCE	389.3	13.88	263	81, 353
$\gamma$ -chlordane	409.8	15.19	272	65, 373
4,4-DDE	318.02	17.38	246	176, 318
Endrin	380.90	18.74	281	263, 345
P,p-DDT	354.49	19.25	212	165, 235
ESS	422.9	21.87	272	229, 387
Dieldrin	380.91	23.28	280	249, 379
MC	345.65	24.88	240	227, 274
DBC	499	25.25	237	99, 388

**Fig. 1.** Schematic diagram of the developed EPA-FOS-DLLME method.

source temperature 230 °C; and quadruple temperature 150 °C; scanning from  $m/z$  45 to 500 at 150 s per scan; and solvent delay time, 3 min. Analysis was performed in the selected ion monitoring (SIM) mode using one quantitative and two qualifier ions. Table 1 summarizes the lists of OCPs, molar mass, retention times, the quantitative and qualifier ions of the studied pesticides.

#### 2.4. EPA-FOS-DLLME procedure

Initially, an appropriate effervescent precursors ratio (CO<sub>2</sub> source: proton donor) and the extraction solvent volume were separately added to 15-mL falcon tube. Then, 10 mL water sample was added to the tube. The effervescent reaction has taken place, generating CO<sub>2</sub> from the bottom of the tube to top and as a result the extraction solvent was rapidly dispersed throughout the aqueous sample. When the reaction was ceased in 2–3 min, the solution was gently shaken and left to stand for about 1 min to obtain a clear phase separation [30]. Afterwards, the lower aqueous phase was carefully discarded using a 10 mL medical syringe to easily transfer the upper phase into auto-sampler vial for the subsequent GC-MS analysis. The schematic diagram of the developed EPA-FOS-DLLME method is shown in Fig. 1.

### 3. Results and discussion

#### 3.1. Optimization of EPA-FOS-DLLME method

To obtain better extraction efficiencies different parameters influencing the EPA-FOS-DLLME procedure were investigated. The

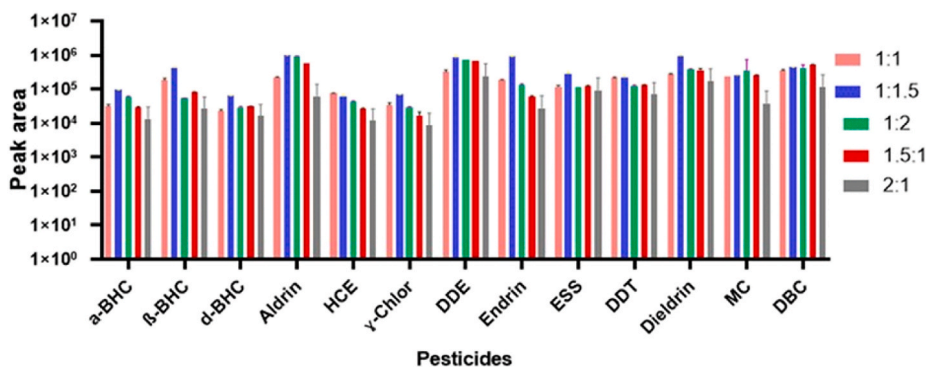


Fig. 2. Effect of the molar ratio of TA:  $\text{Na}_2\text{CO}_3$  on the peak area of OCPs.

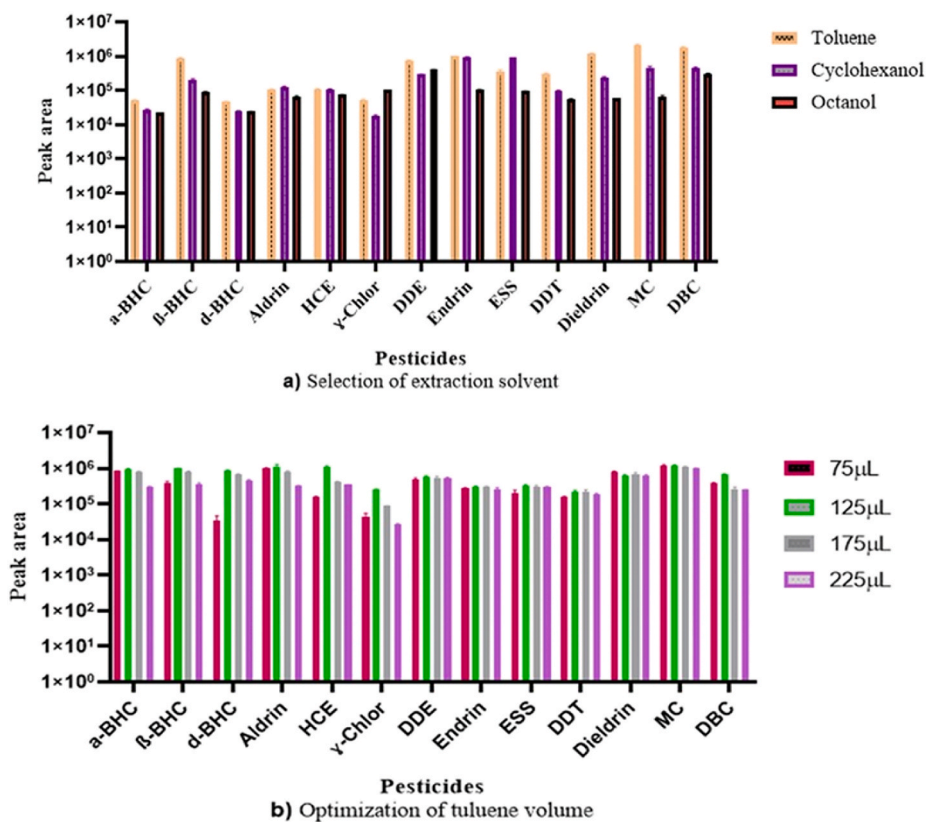


Fig. 3. Effect of (a) extraction solvent type and (b) extraction solvent volume on the peak area of OCPs.

parameters were evaluated using 10 mL water sample containing 40  $\mu\text{g}/\text{L}$  of each OCPs.

### 3.1.1. Effect of the types of $\text{CO}_2$ source and proton donor

Effervescent agents consist of  $\text{CO}_2$  source and proton donor. Different  $\text{CO}_2$  sources including  $\text{K}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  were studied. To choose the appropriate  $\text{CO}_2$  source, each salt was separately mixed with CA as the proton donor based on their stoichiometry in the effervescence reaction. The results showed that  $\text{Na}_2\text{CO}_3$  provided better extraction efficiencies than  $\text{K}_2\text{CO}_3$  and  $\text{NaHCO}_3$ . The variations were observed might be due to their differences in effervescence time and dispersion efficiency. The effervescence time has two opposing effects on the extraction efficiency of EPA-DLLME. Vigorous dispersion and higher extraction efficiency were obtained with longer effervescence time, whereas shorter effervescence time resulted in incomplete dispersion and shorter extraction time, leading to lower extraction efficiency [32]. In the present study,  $\text{Na}_2\text{CO}_3$  showed relatively longer effervescence time and best extraction efficiency and thus, it was selected as  $\text{CO}_2$  source for further studies.

Similarly, acids including CA, OA, and TA were studied as the proton donor. To select the appropriate acid type 0.30 g  $\text{Na}_2\text{CO}_3$  as

**Table 2**

The analytical performance characteristics of EPA- FOS-DLLME combined with GC-MS analysis.

OCPs	Linear range ( $\mu\text{g/L}$ )	$R^2$	LOD ( $\mu\text{g/L}$ )	LOQ ( $\mu\text{g/L}$ )	RSD, Intra-day, n = 6			RSD, Inter-day n = 9			EF
					0.8 $\mu\text{g/L}$	1.6 $\mu\text{g/L}$	2.4 $\mu\text{g/L}$	0.8 $\mu\text{g/L}$	1.6 $\mu\text{g/L}$	2.4 $\mu\text{g/L}$	
$\delta$ -BHC	0.60–2.80	0.9997	0.20	0.60	1.64	1.59	2.25	3.46	1.81	2.86	55
$\beta$ -BHC	0.32–2.80	0.9995	0.09	0.32	1.29	0.62	0.33	2.21	1.35	0.97	42
$\delta$ -BHC	0.60–2.80	0.9996	0.20	0.60	0.83	0.87	0.9	0.96	2.59	1.88	72
Aldrin	0.73–2.80	0.9993	0.24	0.73	2.49	1.58	1.40	3.85	3.67	1.76	24
HCE	0.52–2.80	0.9998	0.17	0.52	1.04	1.25	1.38	2.70	3.71	1.86	67.5
$\gamma$ -Chlordane	0.470–2.80	0.9983	0.23	0.70	1.74	1.74	1.05	3.17	4.95	1.43	107
DDE	0.40–2.80	0.9991	0.13	0.40	3.42	1.04	0.53	5.48	1.09	0.70	293
Endrin	0.75–2.80	0.9996	0.24	0.75	1.66	0.73	0.87	2.73	0.92	4.71	80
DDT	0.26–2.80	0.9996	0.07	0.26	4.47	0.51	0.43	5.52	0.60	0.51	285
ESS	0.59–2.80	0.9981	0.19	0.59	1.36	1.26	1.85	2.03	2.83	2.16	276
Dieldrin	0.57–2.80	0.9981	0.19	0.57	0.96	0.87	0.82	3.26	2.83	0.96	202
MC	0.41–2.80	0.9996	0.03	0.41	1.00	0.46	0.38	2.66	0.98	0.81	182
DBC	0.47–2.80	0.9988	0.15	0.47	1.13	1.52	1.52	1.90	2.04	1.81	124

$\text{CO}_2$  source was used. TA provided the highest extraction efficiencies than CA and OA. The effervescence reaction was very fast when CA was used as a proton donor, resulting in insufficient dispersion of extraction solvent and then, low extraction efficiencies. However, when OA was used the reaction time was long, which may enhance the solubility of the analytes and the extraction solvent in the aqueous sample. Therefore, TA was selected as a proton donor for further studies.

### 3.1.2. Effect of the ratio of $\text{CO}_2$ source and proton donor

The ratio between  $\text{CO}_2$  source and proton donor has great effect on the effervescent reaction and subsequently, on the extraction efficiency of the method. In general, vigorous effervescence is attained by adding either excess  $\text{CO}_2$  source or proton donor. In this work, different molar ratio of TA (proton donor) and  $\text{Na}_2\text{CO}_3$  ( $\text{CO}_2$  source) were studied. Accordingly, the ratios were set at 1:1 (stoichiometric ratio); 1:1.5 and 1:2 (excess  $\text{CO}_2$  source); as well as 1.5:1 and 2:1 (excess proton donor). The best extraction efficiency was achieved when the ratio of TA:  $\text{Na}_2\text{CO}_3$  was 1:1.5 (Fig. 2). The excess  $\text{Na}_2\text{CO}_3$  may help to increase the ionic strength of the solution and thus led to the improved extraction efficiency of the method [32].

### 3.1.3. Effect of the total mass of effervescent agents

Appropriate amount of the effervescent agents should be added to generate sufficient  $\text{CO}_2$  bubbles to evenly disperse the extraction solvent into the sample solution and thus, promote the transfer of analytes to the organic phase. In this study, the total mass of effervescent agents was investigated from 0.1 to 0.9 g, keeping the ratio of TA:  $\text{Na}_2\text{CO}_3$  at 1:1.5. The peak areas of all target analytes increased with the rise of the total mass of the effervescent agents up to 0.5 g and then, slightly decreased upon addition of higher total masses. The observed lower extraction efficiency at total mass >0.5 g might be due to the rise of ionic strength and viscosity of the sample, which subsequently reduces the mass transfer process [22]. Therefore, 0.5 g total mass of effervescent agents was selected for the next work.

### 3.1.4. Effect of extraction solvent type and volume

Selection of appropriate extraction solvent is important parameters since it affects the extraction efficiencies of the method. The extraction solvent should meet criteria such as low melting point, low solubility in the aqueous sample, low density than water, high affinity for the analyte, easily dispersible during the effervescent reaction, and compatibility with GC [32]. Accordingly, the applicability of three low density solvents including toluene, cyclohexanol, and 1-octanol were investigated. The obtained findings (Fig. 3a) demonstrated that the highest extraction efficiencies were attained when toluene was used. Thus, it was chosen as the extraction solvent for further studies.

The volume of the extraction solvent is another important parameter that needs optimization. Different volumes ranging from 75  $\mu\text{L}$  to 225  $\mu\text{L}$  were examined. It was observed that the peak area of OCPs increased with increasing the extraction solvent volume up to 125  $\mu\text{L}$  and then, declined at volumes higher than 125  $\mu\text{L}$ , indicating dilution of the organic phase (Fig. 3b). However, it was difficult to collect the extraction phase when lower than 75  $\mu\text{L}$  volume was used. Therefore, 125  $\mu\text{L}$  toluene was selected as the optimal volume.

### 3.1.5. Effect of NaCl

Addition of appropriate amount of salt increases ionic strength and subsequently, the extraction efficiency of the method. The salting-out effect at higher ionic strength facilitate the transfer of analytes to the extraction phase. However, addition of higher amount of salt increases the viscosity of the sample solution, and thus, reduces the analytes transfer to the extraction phase [27,28]. The effect of the ionic strength was evaluated by adding different amounts of NaCl ranging from 0.00 to 0.07% (w/v) to the sample solution. The findings showed that the peak areas of all OCPs slightly decreased upon addition of NaCl. This might be associated to the rise of the viscosity of the sample solution, which restricts the transfer of the analytes to the extractant. Therefore, the entire procedure was carried out without salt addition.

**Table 3**  
Relative recoveries (%RR  $\pm$  RSD) of three spiked water samples.

Analyte	Spiked conc. in $\mu\text{g/L}$	%RR $\pm$ RSD		
		Tap	River	Well
$\alpha$ -BHC	0.8	106 $\pm$ 0.57	91 $\pm$ 2.25	93 $\pm$ 0.70
	1.6	87 $\pm$ 1.49	103 $\pm$ 2.01	90 $\pm$ 6.95
	2.4	102 $\pm$ 2.65	98 $\pm$ 1.84	79 $\pm$ 1.24
$\beta$ -BHC	0.8	95 $\pm$ 2.42	106 $\pm$ 0.05	98 $\pm$ 1.93
	1.6	76 $\pm$ 3.21	97 $\pm$ 1.21	95 $\pm$ 2.94
	2.4	77 $\pm$ 1.26	85 $\pm$ 3.68	93 $\pm$ 3.62
$\delta$ -BHC	0.8	77 $\pm$ 3.07	96 $\pm$ 4.45	98 $\pm$ 6.14
	1.6	88 $\pm$ 0.6	88 $\pm$ 1.51	91 $\pm$ 3.43
	2.4	116 $\pm$ 3.73	82 $\pm$ 4.7	93 $\pm$ 3.39
Aldrin	0.8	114 $\pm$ 3.2	102 $\pm$ 1.39	89 $\pm$ 4.22
	1.6	82 $\pm$ 0.59	82 $\pm$ 1.58	101 $\pm$ 4.74
	2.4	103 $\pm$ 1.93	89 $\pm$ 2.72	104 $\pm$ 5.89
HCE	0.8	88 $\pm$ 5.72	104 $\pm$ 0.6	99 $\pm$ 1.35
	1.6	86 $\pm$ 3.97	99 $\pm$ 2.86	95 $\pm$ 6.51
	2.4	102 $\pm$ 4.8	97 $\pm$ 3	104 $\pm$ 6.68
$\gamma$ -Chlordane	0.8	84 $\pm$ 3.64	92 $\pm$ 4.36	106 $\pm$ 2.99
	1.6	104 $\pm$ 1.93	95 $\pm$ 0.75	114 $\pm$ 4.30
	2.4	97 $\pm$ 2.32	88 $\pm$ 4.31	98 $\pm$ 3.97
DDE	0.8	101 $\pm$ 1.14	87 $\pm$ 1.83	111 $\pm$ 2.97
	1.6	114 $\pm$ 3.44	101 $\pm$ 3.34	106 $\pm$ 4.86
	2.4	95 $\pm$ 4.57	83 $\pm$ 2.39	96 $\pm$ 5.83
Endrin	0.8	116 $\pm$ 1.67	103 $\pm$ 4.35	106 $\pm$ 2.86
	1.6	110 $\pm$ 1.42	105 $\pm$ 1.66	98 $\pm$ 4.09
	2.4	102 $\pm$ 3.43	109 $\pm$ 1.26	103 $\pm$ 2.12
DDT	0.8	89 $\pm$ 2.16	101 $\pm$ 2.95	98 $\pm$ 7.65
	1.6	103 $\pm$ 1.4	93 $\pm$ 1.67	92 $\pm$ 3.01
	2.4	100 $\pm$ 1.01	99 $\pm$ 3.64	88 $\pm$ 5.39
ESS	0.8	99 $\pm$ 4.31	80 $\pm$ 0.69	102 $\pm$ 3.88
	1.6	110 $\pm$ 1.61	99 $\pm$ 2.24	94 $\pm$ 3.13
	2.4	99 $\pm$ 2.17	86 $\pm$ 2.28	100 $\pm$ 6.09
Dieldrin	0.8	116 $\pm$ 1.46	109 $\pm$ 0.81	111 $\pm$ 4.17
	1.6	104 $\pm$ 3.15	116 $\pm$ 0.61	109 $\pm$ 0.81
	2.4	105 $\pm$ 3.42	111 $\pm$ 2.27	111 $\pm$ 1.82
MC	0.8	114 $\pm$ 0.93	113 $\pm$ 2.2	98 $\pm$ 5.79
	1.6	97 $\pm$ 5.36	99 $\pm$ 1.72	104 $\pm$ 1.76
	2.4	94 $\pm$ 0.65	102 $\pm$ 1.34	99 $\pm$ 0.86
DBC	0.8	105 $\pm$ 1.6	109 $\pm$ 3.52	111 $\pm$ 4.29
	1.6	104 $\pm$ 3.8	105 $\pm$ 1.15	100 $\pm$ 1.10
	2.4	109 $\pm$ 4.2	116 $\pm$ 0.8	113 $\pm$ 0.91

### 3.2. Method validation

Under the optimized experimental conditions, the linear dynamic ranges; limits of detections (LODs) and quantification (LOQ); precisions (intra- and inter-day); and enrichment factor (EF) were evaluated using matrix matched calibration curves at seven concentration levels from (0.4–2.8  $\mu\text{g/L}$ ). Each concentration level was extracted in triplicates and each extract was analyzed in duplicates. The calibration curves were obtained by plotting peak areas versus concentrations of each OCP. Summary of the results are presented in Table 2. The  $R^2$  values of the regression equations of all OCPs were  $\geq 0.998$ , indicating good linearity of the method in the studied concentrations range. The LOD and LOQ were calculated as 3 and 10 times the ratio of standard error of the response to slope of the calibration curve, respectively [33], were ranging from 0.03 to 0.24  $\mu\text{g/L}$  and 0.26–0.75  $\mu\text{g/L}$ , respectively.

Intra- and inter-day precision were investigated by spiking the water samples with OCPs at three concentration levels. For the intra-day precision studies, three replicate samples were spiked and extracted for each concentration level and then, each extract was analyzed in duplicates. The inter-day precision studies were performed for three successive days, by spiking and extracting a sample for each concentration level and then, the extract was analyzed in triplicates. The obtained RSD for intra- and inter-day precisions ranged from 0.33 to 4.47 and 0.51–5.52, respectively, indicating that the method has good precisions.

The EF of the method which was determined from the ratio of the peak areas of the extracted analyte to the peak area of the initial concentration of the standard analyte spiked in to the sample were ranged 24–293.

### 3.3. Analysis of water samples

Tap, River and Well water samples were used to evaluate the applicability and matrix effects on the extraction of target OCPs. Tap water was collected from Jimma University Analytical Chemistry Lab after free flowing for about 10 min. Well and River water samples were collected from Kochi area, and Awetu River, Jimma town, respectively. Water samples were filtered using Whatman filter paper



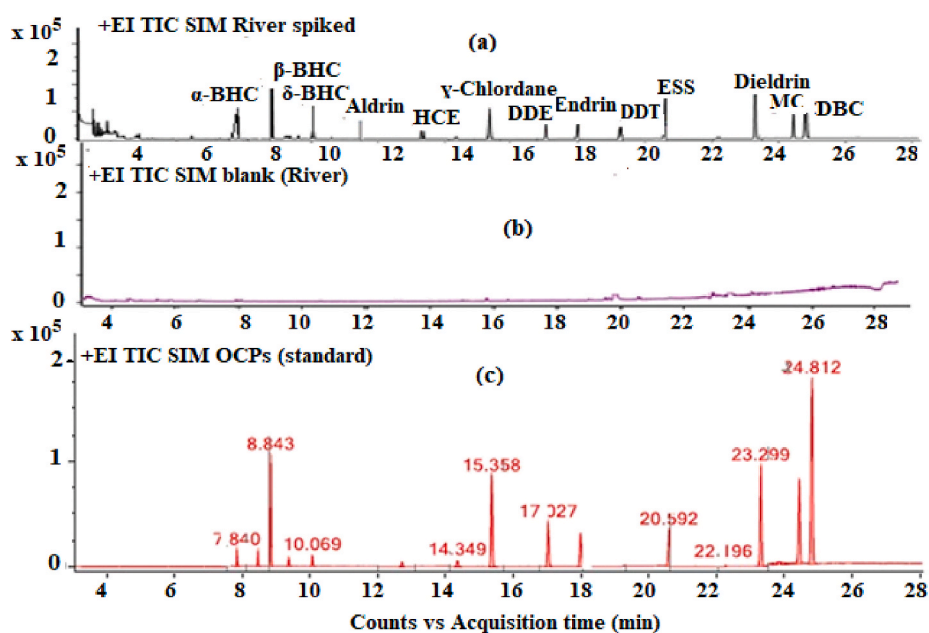


Fig. 4. Representative chromatograms of (a) spiked River water samples, (b) blank (unspiked), and (c) OCPs standards.

prior to using EPA-FOS-DLLME for extraction of the target analytes. None of these OCPs were detected in the water samples. To evaluate the matrix effects, the water samples were spiked with the target OCPs at three concentration levels earlier used for precision studies. The obtained relative recoveries (%RR) were ranged from 76 to 116, 82–109 and 79–114%, for Tap, River, and Well water samples, respectively (Table 3), which are all in acceptable range for analysis of OCPs in such samples [34]. Representative chromatograms of unspiked and OCPs spiked river water samples as well as chromatogram of OCPs standards are displayed in Fig. 4.

### 3.4. Comparison of the proposed method with other reported methods

The proposed EPA-FOS-DLLME was compared with other methods, which were reported for extraction of OCPs from water samples and other related matrices. The comparison was made based on extraction solvent type,  $R^2$ , LOD, RSD, %RR, EF and centrifugation time (Table 4). The proposed method exhibited comparable analytical performance characteristics with reported methods. However, unlike other methods, EPA-FOS-DLLME does not involve centrifugation step. Therefore, EPA-FOS-DLLME could be used as simple, fast, effective and environmentally green alternative for extraction and pre-concentration of OCPs from water samples prior to their quantitative analysis by GC-MS.

## 4. Conclusion

In this paper, EPA-FOS-DLLME has been proposed for the extraction and pre-concentrations of OCPs from water samples prior to their quantitative determinations by GC-MS, in the SIM mode. The extraction solvent, toluene, was dispersed by  $\text{CO}_2$  bubbles *in-situ* generated from the effervescence reaction between the mixture TA and  $\text{Na}_2\text{CO}_3$  powder in the aqueous sample. The method demonstrated good and acceptable analytical performance characteristics for analysis of OCPs from water samples. The method does not use centrifugation, use less toxic extraction solvent and easily accessible effervescent precursors. It also showed comparable, and in some cases, superior analytical performance characteristics than other reported sample preparation methods used for determination of OCPs from water samples. In conclusion, the proposed EPA-FOS-DLLME method could be used as an ease and attractive alternative for extraction and/or pre-concentration of OCPs in water samples and other related matrices.

### Author contribution statement

Kero Assefa Ago, Abera Gure: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; wrote the paper.

Shimeles Addisu Kitte, Gadisa Chirfa: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

**Table 4**  
Comparison of the proposed method with other methods used in pre-concentration and determination of OCPs.

Matrices	Analyte	Analysis method	Extraction solvent	Centrifuga-tion (min)	LOD ( $\mu\text{g/L}$ )	%RR	RSD	R <sup>2</sup>	EF	Ref
Water samples	OCPs	DLLME-GC/MS	Tetrachloro-ethylene	No	0.02–0.06	84–125	7.8–11.7	0.995–0.999	21–185	[19]
River water samples	OCPs and PAH	SPE-GC/ECD	Methanol dichloromethane, hexane	No	–	–	–	–	–	[35]
Cocoa samples	OCPs	CHLLE*-DLLME	Acetonitrile	Yes (5)	0.024–0.041	50–89	<8.9	>0.997	50–89	[36]
Water and fruit samples	OCPs	GC-ECD HLLME	Chloroform	Yes (3)	0.001–0.03	–	4.9–8.6	$\geq 0.994$	486–1090	[37]
Fish	OCPs	GC-ECD QuEChERS DLLME	1-Undecanol	Yes (5)	0.00065–0.0015	88.1–121.2	<15	$\geq 0.994$	–	[38]
Vegetable Samples	OCPs	Fe <sub>3</sub> O <sub>4</sub> MNPs QuEChERS DLLME-GC/MS	Chloroform	Yes (3)	0.15–0.32	78.6–107.7	<7.5	$\geq 0.996$	22.8–36.6	[39]
Tap, River and Well water	OCPs	EPA-DLLME GC/MS	Toluene	No	0.03–0.24	76–116	0.33–5.52	0.9987–0.9997	24–293	Present work

\*Combination of homogeneous liquid-liquid extraction.



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## Data availability statement

The data that has been used is confidential.

## Declaration of interest's statement

The authors declare no conflict of interest.

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