Water with low concentration of surfactant in dispersed solvent-assisted emulsion dispersive liquid–liquid microextraction for the determination of organochlorine pesticides in aqueous samples

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ABSTRACT

A novel sample preparation method, “water with low concentration of surfactant dispersive liquid–liquid microextraction (WLSEME)”, coupled with gas chromatography using an electron capture detector (GC-ECD) was developed for the analysis of the organochlorine pesticides (OCPs), heptachlor, α-endosulfan, 4,4-DDE, 2,4-DDD and endrin, in aqueous samples. A microsyringe is used to withdraw and discharge 10–12 μL of the extraction solvent and 60–120 μL of water as the dispersed solvent (containing 1 mgL⁻¹, Tween 80) 4 times within 10 s to form a cloudy emulsified solution in the syringe. This is then injected into an 8 mL aqueous sample spiked with all above OCPs. Dodecyl acetate and 2-dodecanol were both selected as extraction solvents to optimize their conditions separately. The total extraction time was about 0.5 min. Under optimum conditions, using dodecyl acetate (12 μL) as extraction solvent, the linear range of the method was 10–1000 ng L⁻¹ for all OCPs, and the limits of detection (LODs) ranged from 1 to 5 ng L⁻¹. The absolute recoveries and relative recoveries were from 20.8 to 43.5% and 83.2 to 109.8% for lake water, and 19.9–49.2% and 85.4–115.9% for seawater respectively. In the second method, 2-dodecanol as extraction solvent, the linear range was from 5 to 5000 ng L⁻¹ for the target compounds, and the LODs were between 0.5 and 2 ng L⁻¹. The absolute recoveries and relative recoveries ranged from 25.7 to 42.2% and 96.3–111.3% for sea water, and 22.4–41.9% and 90.7–107.9% for stream water. This could solve several problems, which commonly occur in ultrasound-assisted emulsification micro-extraction (USEME), dispersive liquid–liquid micro-extraction (DLLME) and other assisted emulsification methods. These problems include analyte degradation, increased solubility of the extraction solvent and analyte, and high toxicity and large volume of the organic solvent used.

1. Introduction

From 1950 to 1970, organochlorine pesticides (OCPs) were widely used to combat pests in agriculture and industry, and to control diseases. However, OCPs are in the class of persistent organic pollutants (POPs). Because of the toxicity and persistence of OCPs, long-term consumption of food containing these pesticides leads to the risk of chronic poisoning, malformations, cancer, and genetic variation. OCPs also act as environmental hormones, which affect the human endocrine system and hinder reproductive and growth functions on long-term exposure [1]. In 2001, the United Nations environment programme (UNEP) established the Stockholm convention to restrict the use of some OCPs, but their physicochemical properties make them very resistant to degradation in the environment. They are therefore very widely distributed in the environment. As some OCPs are highly lipophilic compounds, they easily accumulate in the environmental matrix or cause bioaccumulation, which results in biomagnifications through direct uptake in the food chain. OCPs are still widely detected in a broad range of natural samples [2–4]. The development of reliable sample pretreatments is essential for the determination of these compounds at trace levels. Most OCPs determinations require preparative processes, such as liquid–liquid extraction (LLE), solid-phase extraction (SPE), or microwave-assisted solvent extraction (MASE) [5]. These methods use large amounts of organic solvents and are time-consuming. To avoid these difficulties, solid-phase micro-extraction (SPME) [6–8] has been developed. Although SPME does not use an extraction solvent, it is time-consuming and labor-intensive. Recently, several improved liquid phase micro-extraction (LPME) techniques having high extraction efficiencies.
have been reported [9–14]. They have led to enhancement of the sensitivity and improvement of the ruggedness of LPME using less extraction solvent but all require lengthy extraction times.

In comparison to conventional methods, the consumption of organic extraction solvent in dispersive liquid–liquid microextraction (DLLME) [15] is significantly lower, its extraction time is shorter, and much higher enrichment of analytes is obtained. However, the high-density extraction solvent used, typically chlorobenzene, chloroform, or carbon tetrachloride, is highly toxic. Lately the solidification of a floating organic drop (DLLME-SFO) [16], ultrasound-assisted emulsification [17] and low-density extraction solvents [18,19] have been introduced to DLLME. Those techniques use a halogen-free extraction solvent of low toxicity and retain the advantages of DLLME, but still require a large amount of organic solvent as dispersed solvent. Although ultrasoundization improves the emulsification without adding dispersed solvent, it may result in the degradation of pesticides [20].

To replace dispersed solvent and other assisted emulsification methods, surfactants, soluble in both organic solvents and water, are an alternative in DLLME. The level of lipophilic or hydrophilic tendency of a surfactant can be decided by its hydrophile–lipophile balance (HLB) [21]; the greater the HLB value the stronger the hydrophilic lipophilic character of the surfactant. Since the electrostatic, hydrophilic, and hydrophobic characteristics of surfactants vary, different surfactants may be most effective oil–in-water emulsifiers with analytes of different character [22–24]. This ability has been used to develop methods for the extraction and preconcentration of analytes [25–31] and for bio-analysis of different basic drugs as model analytes [21]. However, these methods require relatively high surfactant concentrations.

The objective of this study was to improve on DLLME, which uses a large amount of dispersed solvent, to develop a technique using water with a low concentration of surfactant in dispersed solvent-assisted emulsion dispersive liquid–liquid micro-extraction (WLSEME) combined with an improved solvent collection system (ISCS) [28] to extract OCPs in aqueous samples.

2. Experimental

2.1. Reagents and samples

All pesticides were purchased as 100 mg L\(^{-1}\) solutions of reagent grade pesticide. Heptachlor was purchased from Fluka (Buchs, Switzerland). \(\alpha\)-Endosulfan was purchased from RDH (Seelze-Hannover, Germany). 4,4-DDE and 2,4-DDD were purchased from Chem Service (West Chester, Pennsylvania, USA). Endrin was purchased from Applied Separations (Allentown, Pennsylvania, USA). Stock standard solutions of the pesticides were prepared in methanol at concentration of 1 mg L\(^{-1}\) and stored at 4°C. Working solutions (1 \(\mu\)g L\(^{-1}\)) used to optimize the parameters of WLSEME were prepared weekly. Methanol and acetone were HPLC-grade and obtained from Echo (Miaoli, Taiwan).

The extraction solvents (p-xylene, \(\alpha\)-xylene, m-xylene, decane, dodecane and tetradecane) were purchased from Fluka (Buchs, Switzerland). 1-Octanol, 1-nonanol, 1-decanol, 1-undecanol, 1-dodecanol and 2-dodecanol were purchased from Merck (Darmstadt, Germany). Hexadecane and dodecyl acetate were purchased from Sigma–Aldrich (Missouri, USA). Deionized water (DI water) was obtained from Millipore (Bedford, Massachusetts, USA) Milli-Q water purification system.

The surfactants (Triton X-100, Tween 20) were purchased from Sigma–Aldrich (Missouri, USA). Triton X-114 and Tween 80 were purchased from J.T. Baker (TX, USA). The lake water samples (Hsinchu, Taiwan), sea water sample (Hsinchu, Taiwan) and stream water sample (Hsinchu, Taiwan) were filtered through a 0.45 \(\mu\)m membrane (Millipore, Bedford, Massachusetts, USA) prior to extraction.

2.2. Instrumentation

A Hewlett-Packard gas chromatograph (Minnesota, USA) 5890 Series equipped with an electron capture detector (ECD) operated at 320 °C, and a DB-608 fused silica capillary column (30 m \(\times\) 0.53 mm \(\times\) 0.83 \(\mu\)m, J&W Scientific, California, USA) was employed for the determination of OCPs. Helium (purity 99.999%) was used as carrier gas (flow rate: 3 mL min\(^{-1}\)) and nitrogen (purity 99.9995%) was used as makeup gas (flow rate 30 mL min\(^{-1}\)). The column oven was initially held at 170 °C, and the temperature then increased to 230 °C at 3 °C min\(^{-1}\); the temperature was subsequently increased to 245 °C at 3 °C min\(^{-1}\); it was then increased to 273 °C at 3 °C min\(^{-1}\) and held at that temperature for 6 min. The injector temperature was 240 °C. The ISCS system is to use a microtube designed in-house (15 mm \(\times\) 3 mm, inner diameter: 1.8 mm; from Qing-Fa Company, Hsinchu, Taiwan) to separate the aqueous and organic phases. The total volume of the microtube is approximately 38 \(\mu\)L. An ultrasonic cleaner 5510 (40 kHz, Branson, USA), vortex-genie\(^\text{®}\) 2 mixer equipped with pop-off cup (Scientific Industries, New York, USA), FS-6 Funnel shaker (Sun-way, Hsinchu, Taiwan) and Centrifuge CN-2200 (Hsiantai Machinery Industry, Hsinchu, Taiwan) were utilized in the proposed method.

2.3. Extraction procedure

The experimental procedure for using water with low concentrations of surfactant in the dispersed solvent-assisted emulsion dispersive liquid–liquid microextraction (WLSEME) method is illustrated in Fig. 1. A mixture of 10–12 \(\mu\)L extraction solvent (dodecyl acetate and 2-dodecanol) and 60–120 \(\mu\)L of water as a dispersed solvent (containing 1 mg L\(^{-1}\) of Tween 80) was prepared in an eppendorf. After a microsyringe was used to pump the mixture back and forth 4 times within a period of 10 s a cloudy emulsified solution was formed. This was then injected into an 8 mL portion of the aqueous sample spiked with 1 \(\mu\)g L\(^{-1}\) of the analytes. The tube containing the sample was then centrifuged at 5000 rpm for 3 min. After centrifugation, the superfluent organic microdroplet (1 \(\mu\)L) was transferred into a microtube (15 mm \(\times\) 3 mm) with a syringe. The organic phase was easily collected and recovered in the upper portion of the microtube and 1 \(\mu\)L of extractant was injected into the GC-ECD system for analysis.

3. Results and discussion

3.1. Impact of solvent on extraction efficiency

The selection of extraction solvent is an important parameter for the extraction efficiency. The properties of solvents should be compatible with following: (1) immiscible with water; (2) low toxicity and (3) good solubility for the analytes. For the application of the above conditions (1) xylenes: \(\alpha\)-xylene, \(m\)-xylene and \(p\)-xylene, (2) alcohols: 1-octanol, 1-nonanol, 1-decanol, 1-undecanol, 1-dodecanol and 2-dodecanol, (3) alkanes: decane, dodecane, tetradecane and hexadecane, and (4) esters: dodecyl acetate were tested. The results are shown in Fig. 2. The experiment revealed that 1-dodecanol has better enrichment factors than the other solvents. However, it is not suitable to use when the room temperature is below its melting point (24.0 °C). Therefore, dodecyl acetate, which yielded the second highest enrichment factor, and 2-dodecanol, which also had high enrichment factors and better precision, were both chosen as the extraction solvent and tested in the following study.
3.2. Volume of extraction solvent

To determine the optimal volume of dodecyl acetate, a series of volumes (dodecyl acetate: 10, 12, 14, 16 and 18 μL; 2-dodecanol: 8–10, 12 and 16 μL) were examined. The enrichment factors which were obtained from both solvents decreased with adding more extraction solvents. The results support that extractant was diluted as a result of the increased volume of the floating phase. However, if only a small amount of the extraction solvent was added, the final volume of floating solvent was too low to withdraw into the microsyringe. To address this issue, 12 μL of dodecyl acetate and 10 μL of 2-dodecanol were used for further study.

3.3. Type of surfactant

The selection of surfactant is of crucial importance in the proposed method as they are soluble in both extraction solvent and water. This makes them be commonly used to improve the dispersion of extraction solvents. A surfactant with high hydrophile–lipophile balance (HLB) value has higher hydrophilicity. When the HLB value of a surfactant is between 12 and 16, the surfactant is considered as an emulsifier-assisted oil–water emulsifier. Two kinds of well-known polyoxyethylene-type nonionic surfactants, Tween and Triton were studied in Fig. 3. The HLBs of Triton X-100, Triton X-114, Tween 20 and Tween 80 are 13.4, 12.3, 16.7 and 15.0, respectively. Based on the experimental results, Tween 80, which had the highest extraction efficiency was selected as the dispersed solvent.

3.4. Volume of the surfactant solution

To investigate the impact of volume of the aqueous solution, different volumes of aqueous solution (dodecyl acetate: 60, 120, 180, and 240 μL; 2-dodecanol: 30, 60, 120 and 180 μL) containing 1 mg L⁻¹ Tween 80 were evaluated. When the volume of aqueous solution was changed from 60 to 120 μL for dodecyl acetate and 30–60 μL for 2-dodecanol, the extraction enrichment factors were increased. On the other hand, the enrichment factors decreased on increasing the volume of aqueous solution from 120 to 240 μL for dodecyl acetate and 60–180 μL for 2-dodecanol. Therefore, the
volume of aqueous solution was fixed at 120 μL for dodecyl acetate. The concentration of surfactant was approximately equivalent to 0.015 mg L⁻¹ in the total 8 mL of sample solution. For 2-dodecanol, 60 μL of surfactant volume was selected and its concentration was approximately 0.007 mg L⁻¹.

3.5. Concentration of the surfactant

The concentration of surfactant in aqueous solution plays an important role on effective extraction. The influence of the Tween 80 concentration was investigated by studying the results obtained with concentration of 0–4 mg L⁻¹. As shown in Fig. 4, when the concentration of surfactant in the aqueous solution was increased from 0 to 1 mg L⁻¹, the extraction enrichment factor was dramatically improved. However, the enrichment factors declined with spiking tween 80 over 1 mg L⁻¹. It is evident that adding higher concentrations of Tween 80 may increase the solubility of analytes in aqueous solutions. This may result in lower enrichment factors. On the basis of the above observations, the optimal concentration of surfactant in the aqueous solution was selected as 1 mg L⁻¹ for both dodecyl acetate and 2-dodecanol.

3.6. Performances of WLSEME and other dispersive techniques

In order to demonstrate the performance of WLSEME with dodecyl acetate and 2-dodecanol, other dispersive methods such as ultrasound-assisted, manual shaking before ultrasound-assisted, vortex and up and down shaker emulsification were compared with the proposed method. The extraction solvent (dodecyl acetate), solvent volume (12 μL) and sample volume (8 mL) were the same for each method mentioned above. Only the extraction time was optimized individually. The optimal time was 2 min for ultrasound-assisted, 3 min for manual shaking before ultrasound-assisted, 3 min for vortex and 2 min for up and down shaker-assisted emulsion, respectively. Fig. 5 showed that enrichment factors were obtained by these six approaches. WLSEME with 12 μL of dodecyl acetate had the highest enrichment factor among the examined emulsification methods. 10 μL of 2-dodecanol for WLSEME had the second highest enrichment factor and better precision. This demonstrated that WLSEME was able to generate homogeneous and fine droplets quickly which led to rapid partition of analytes between extraction solvent and aqueous phase. It consequently resulted in high enrichment factors.

Fig. 3. Effect of the type of surfactant for the first extraction solvent (n = 3). Samples were spiked with 1 μg L⁻¹ of each analyte. Extraction conditions: extraction solvent dodecyl acetate; volume 12 μL; dispersed solvent volume 60 μL; concentration of the surfactant, 1 mg L⁻¹.

Fig. 4. Effect of the concentration of the surfactant as dispersed solvent for the second extraction solvent (n = 3). Samples were spiked with 1 μg L⁻¹ of each analyte. Extraction conditions: extraction solvent, 2-dodecanol volume, 10 μL; dispersed solvent: Tween 80 volume, 60 μL.
Table 1
The linear range (LR), method detection limit (MDL), limit of quantification (LOQ), precision (RSD), and enrichment factor (EF) of the first proposed method using 12 μL of dodecyl acetate (DA) and 10 μL of 2-dodecanol (2-D).

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Linear rangea (ng L⁻¹)</th>
<th>Coefficient of determination (R²)</th>
<th>MDLs (ng L⁻¹)</th>
<th>LOQs (ng L⁻¹)</th>
<th>RSD(%) (intraday)</th>
<th>RSD(%) (interday)</th>
<th>EF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DA</td>
<td>2-D</td>
<td>DA</td>
<td>2-D</td>
<td>DA²</td>
<td>2-D³</td>
<td>DA²</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>5–5000</td>
<td>1–5000</td>
<td>0.9972</td>
<td>0.9970</td>
<td>2</td>
<td>0.5</td>
<td>1.29</td>
</tr>
<tr>
<td>α-Endosulfan</td>
<td>5–5000</td>
<td>2–10,000</td>
<td>0.9969</td>
<td>0.9999</td>
<td>2</td>
<td>1.0</td>
<td>10.4</td>
</tr>
<tr>
<td>4,4-DDE</td>
<td>5–1000</td>
<td>1–10,000</td>
<td>0.9963</td>
<td>0.9994</td>
<td>1</td>
<td>0.5</td>
<td>9.2</td>
</tr>
<tr>
<td>2,4-DDD</td>
<td>10–5000</td>
<td>2–5000</td>
<td>0.9990</td>
<td>0.9986</td>
<td>5</td>
<td>1.0</td>
<td>12.3</td>
</tr>
<tr>
<td>Endrin</td>
<td>10–5000</td>
<td>5–5000</td>
<td>0.9985</td>
<td>0.9990</td>
<td>5</td>
<td>2.0</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Heptachlor: 1, 5, 10, 50, 100, 500, 1000, 2500 and 5000 ng L⁻¹.
α-Endosulfan: 2, 5, 10, 50, 100, 500, 1000, 5000 and 10,000 ng L⁻¹.
4,4-DDE: 1, 5, 10, 50, 100, 500, 1000, 5000 and 10,000 ng L⁻¹.
2,4-DDD: 2, 5, 10, 50, 100, 500, 1000, 2000 and 5000 ng L⁻¹.
Endrin: 5, 10, 50, 100, 500, 1000, 2000 and 5000 ng L⁻¹.

a Calibration curve with concentration.
b Water sample spiked with 5 ng L⁻¹ for Heptachlor, α-Endosulfan and 4,4-DDE; 10 ng L⁻¹ for 2,4-DDD and Endrin, respectively (n = 7).
c Water sample spiked with 5 ng L⁻¹ for all compounds (n = 7).

Table 2
Absolute recoveries (AR), relative recoveries (RR) and precision (RSD) of OCPs in spiked lake water and spiked sea water samples using 10 μL of 2-dodecanol.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Spiked (ng L⁻¹)</th>
<th>Sea water</th>
<th>Stream water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AR (%)</td>
<td>RR (%)</td>
<td>RSD (%)</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>30.5</td>
<td>105.5</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>37.4</td>
<td>96.3</td>
</tr>
<tr>
<td>α-Endosulfan</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>37.4</td>
<td>96.3</td>
</tr>
<tr>
<td>4,4-DDE</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>26.1</td>
<td>111.2</td>
</tr>
<tr>
<td>2,4-DDD</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>38.6</td>
<td>103.2</td>
</tr>
<tr>
<td>Endrin</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>32.4</td>
<td>96.3</td>
</tr>
</tbody>
</table>

ND: no detected.
Table 3
Comparison with other extraction methods using GC-ECD.

<table>
<thead>
<tr>
<th>Extraction methods</th>
<th>Extraction solvent/dispersed solvent (LD50, mg kg(^{-1}) [Rat])</th>
<th>Solvent volume (μL)</th>
<th>Extraction time (min)</th>
<th>Sample volume (mL)</th>
<th>Compound</th>
<th>LODs (ng L(^{-1}))</th>
<th>Disadvantages</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPME</td>
<td>-</td>
<td>0</td>
<td>120</td>
<td>35</td>
<td>Heptachlor α-Endosulfan p,p’-DDE, Endrin</td>
<td>500 300 100 200</td>
<td>Long extraction time, large sample volume and high LODs</td>
<td>[6]</td>
</tr>
<tr>
<td>MA-HS-SPME(^a)</td>
<td>-</td>
<td>0</td>
<td>10</td>
<td>20</td>
<td>Heptachlor α-Endosulfan p,p’-DDE, Endrin</td>
<td>2–70</td>
<td>Large sample volume and high LODs</td>
<td>[8]</td>
</tr>
<tr>
<td>HF-LPME(^b)</td>
<td>Toluene (636)</td>
<td>5</td>
<td>30</td>
<td>5</td>
<td>Heptachlor α-Endosulfan, Endrin</td>
<td>30 28 33</td>
<td>Long extraction time and high LODs</td>
<td>[12]</td>
</tr>
<tr>
<td>DHT-LPME(^c)</td>
<td>1-Hexanol (720)</td>
<td>48</td>
<td>30</td>
<td>10</td>
<td>Heptachlor α-Endosulfan p,p’-DDE</td>
<td>2 5 4</td>
<td>Long extraction time and high LODs</td>
<td>[14]</td>
</tr>
<tr>
<td>DLLME-SFO</td>
<td>Hexadecane (→)/acetone (5800)</td>
<td>10/500</td>
<td>7</td>
<td>5</td>
<td>Heptachlor Aldrin α-Endosulfan p,p’-DDE</td>
<td>85.9 29.2 19.7 15.8</td>
<td>Long extraction time and high LODs</td>
<td>[16]</td>
</tr>
<tr>
<td>USAEME(^d)</td>
<td>1-Decanol (4720)</td>
<td>10</td>
<td>4</td>
<td>10</td>
<td>Heptachlor α-Endosulfan p,p’-DDE o,p’-DDD</td>
<td>0.6 1.1 2.9 2.7</td>
<td>Long extraction time</td>
<td>[17]</td>
</tr>
<tr>
<td>WUSEME</td>
<td>Dodecyl acetate (&gt;5000)/water (1.2 × 10(^{-7}) g Tween 80)</td>
<td>12/120</td>
<td>0.5</td>
<td>8</td>
<td>Heptachlor α-Endosulfan p,p’-DDE o,p’-DDD Endrin</td>
<td>2 1 5 5</td>
<td>-</td>
<td>The proposed method</td>
</tr>
<tr>
<td>WUSEME</td>
<td>2-Dodecanol (→)/water (6 × 10(^{-8}) g Tween 80)</td>
<td>10/60</td>
<td>0.5</td>
<td>8</td>
<td>Heptachlor α-Endosulfan p,p’-DDE o,p’-DDD Endrin</td>
<td>0.5 1 5</td>
<td>-</td>
<td>The proposed method</td>
</tr>
</tbody>
</table>

\(^a\) MA-HS-SPME: microwave-assisted headspace solid-phase microextraction.
\(^b\) HF-LPME: hollow fiber–liquid phase microextraction.
\(^c\) DHT-LPME: dynamic hook-type liquid-phase microextraction.
\(^d\) USAEME: ultrasound-assisted emulsification microextraction.
3.7. Quantitative aspects

The linearity using 12 μL of dodecyl acetate was evaluated under optimum conditions. Calibration curves were exhibited at different concentrations ranging from 5 to 5000 ng L⁻¹ in the D.I. water (5, 10, 50, 100, 500, 1000, 2000, 2500, and 5000 ng L⁻¹); these yielded coefficients of determination higher than 0.9963 for all OCPs. The data on linear range (LR), coefficient of determination ($R^2$), limits of detection (LODs), limit of quantifications (LOQs), precision (RSD), and enrichment factor (EF) were summarized in Table 1. It revealed that the RSD values were below 12.9% based on the peak areas from seven replicate runs. The coefficients of determination of the calibration curves ($R^2$) were in the range of 0.9963–0.9990, which indicated that there was good linearity within these concentration ranges for each analyte. The values of LODs were calculated as three times the standard deviation of seven replicate runs of D.I. water spiked at low concentrations of the analytes. The LODs of OCPs in the aqueous sample differed substantially and ranged from 2 to 5 ng L⁻¹. The intraday RSDs for the five analytes were 6.1–12.9%. The interday RSDs were 9.7–14.4%. The enrichment factor, defined as the ratio between the final (equilibrium) concentration of the analyte in the organic phase and the initial concentration of the analyte in the aqueous sample, were between 1901 and 3530. High enrichment factors were achieved by this method.

10 μL of 2-dodecanol was also selected as extraction solvent to validate the proposed study. Under optimum conditions, calibration curves ranged from 1 to 10,000 ng L⁻¹ in the D.I. water (1, 2, 5, 20, 100, 500, 1000, 5000, and 10,000 ng L⁻¹). The LODs of OCPs were between 0.5 and 2.0 ng L⁻¹, and the LOQs ranged from 1 to 5 ng L⁻¹. The interday RSDs were from 5.0 to 10.3%; the RSDs of intraday ranged from 4.0 to 5.1%. Enrichment factor (EF) values were between 1881 and 3108.

3.8. Environmental sample analysis

To demonstrate the capability of the first solvent, 12 μL of dodecyl acetate, the procedure was applied to the analysis of OCPs in lake and sea waters. The results showed that the analyzed samples were free of OCPs. The water samples were spiked with the analytes at 50, 500, and 5000 ng L⁻¹ levels. The absolute recoveries for the five OCPs were between 20.8 and 43.5% for lake water and 19.9–49.2% for sea water; the relative recoveries were between 83.2 and 109.8% for lake water and 85.4 and 115.9% for sea water respectively; RSDs for the five analytes ranged from 7.1 to 14.8% for lake water and 3.0–13.6% for sea water.

For 2-dodecanol, the absolute recoveries, relative recoveries and RSDs of the five OCPs at the two spiked different concentration levels (100 and 500 ng L⁻¹) were carried out for sea and stream water samples. Table 2 shows the recoveries and RSDs for sea and stream water samples. The absolute recoveries ranged from 25.7 to 42.2% for sea water and 22.4–41.9% for stream water. The relative recoveries were from 96.3 to 111.2% for sea water and 90.7–107.9% for stream water individually. The RSDs for the five analytes were 1.2–8.5% for sea water and 1.4–6.4% for stream water. This implies that there was no significant interference for the determination of OCPs. The proposed method was not affected seriously by the sample matrices. Compared with other extraction methods (Table 3), the present study uses low toxic and halogen-free solvent to extract target analytes. The extraction time of this method is 0.5 min, which is shorter than most of other methods, and the LODs are the best of the listed methods. It required only 0.015 or 0.007 mg L⁻¹ of surfactants without large amounts of dispersed solvent, which is usually needed in DLLME.

4. Conclusions

This is the first time using water with a low concentration of surfactant as dispersed solvent combining the ISCS technique to extract analytes from aqueous solution. Only 0.015 and 0.007 mg L⁻¹ of surfactants were required in the study. Compared with those methods using several mg L⁻¹ of surfactants, the concentrations applied here were approximately a thousand time lower and the extraction efficiency obtained was higher. Moreover, this method employed few micro-liter of low toxicity, halogen-free organic solvents to extract OCPs. This study provided an alternative to solve the common problems in the USAEME, DLLME and other assisted emulsification methods, including analyte degradation, increased solubility of the extraction solvent and analyte in aqueous solution, usage of toxic extraction solvents and large volumes of dispersed solvent. In addition, the experimental results demonstrated wide linear ranges, well LODs, and good precision, enrichment factor and relative recovery. The method is a desirable application for separation and pre-concentration of OCPs at trace levels in aqueous samples.

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References
