Analytical Methods

Application of elevated temperature-dispersive liquid-liquid microextraction for determination of organophosphorus pesticides residues in aqueous samples followed by gas chromatography-flame ionization detection

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- Malathion (PubChem CID: 4004)
- Chlorpyrifos (PubChem CID: 2730)
- Profenofos (PubChem CID: 4004)
- Phosalone (PubChem CID: 4793)

Keywords:
- Organophosphorous pesticides
- Elevated temperature dispersive liquid-liquid microextraction
- Gas chromatography
- Aqueous sample

A B S T R A C T

In the present study, an elevated temperature, dispersive liquid-liquid microextraction/gas chromatography-flame ionization detection was investigated for the determination, pre-concentration, and extraction of six organophosphorus pesticides (malathion, phosalone, dichlorvos, diazinon, profenofos, and chlorpyrifos) residues in fruit juice and aqueous samples. A mixture of 1,2-dibromoethane (extraction solvent) and dimethyl sulfoxide (disperser solvent) was injected rapidly into the sample solution heated at an elevated temperature. Analytical parameters, including enrichment factors (1600–2075), linearity (r > 0.994), limits of detection (0.82–2.72 ng mL⁻¹), and quantification (2.60–7.36 ng mL⁻¹), relative standard deviations (<7%) and extraction recoveries (64–83%), showed the high efficiency of the method developed for analysis of the target analytes. The proposed procedure was used effectively to analyse selected analytes in river water and fruit juice, and diazinon was found at ng mL⁻¹ concentrations in apple juice.

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1. Introduction

Organophosphorus pesticides (OPPs) are applied extensively throughout the world due to their wide activity against pests and relatively low cost. They are also gradually replacing organochlorine pesticides due to their low environmental persistence (You, Xing, Liu, & Jiang, 2013; Lin, Huang, & Liu, 2006). Generally, OPPs are used for different classes of vegetables, grain crops and fruits (Jalali, Balali-Mood, Jalali, & Shakeri, 2012) to enhance quality and yield. Frequently, pesticides are used during the growth period and, sometimes, at the fruiting phase. OPPs are an important source of environmental contamination due to their widespread use (Padrón-Sanz et al., 2005; Tsoukali, Theodoridis, Raikos, & Grigoratou, 2005) and contaminate agricultural products, such as fruit juices. OPPs penetrate the crop matrices and are converted to compounds that are toxic for human (Yao, Jiang, Liu, & Cheng, 2001). Neurological symptoms are the most reported effects of OPPs toxicity. For example, OPPs inhibit the acetyl-cholinesterase function in the transmission of nerve-impulse (Maroni, Colosio, Ferioli, & Fait, 2000). Other effects have not been well studied, but are...
important in risk assessment. European Union regulations have defined maximum residue limits (MRLs) for OPPs in food and water samples in the range 0.01–0.5 mg kg\(^{-1}\) and 20–100 µg L\(^{-1}\), respectively [http://ec.europa.eu/sanco-pesticides/public/event=homepage]. Thus, development of a simple, rapid, sensitive method to detect the residues of pesticides in foods is important.

Several analytical methods have been developed for the determination of OPPs in aqueous samples, such as high-performance liquid chromatography (HPLC) (Farajzadeh, Bahram, Vardast, & Bamorowat, 2011), capillary electrophoresis (CE) (Li, Zhou, Jin, Zhang, & Liu, 2010), and gas chromatography (GC) (Bidari, Ganjali, Norouzi, Hosseini, & Assadi, 2011). However, to concentrate and isolate the compounds of interest, sample preparation step is generally required. Traditionally, extraction and enrichment of analytes are usually done by solid phase extraction (SPE) (Wang & Du, 2010; De la Colina, Peña Heras, Díos Cannela, & Sánchez Rasero, 1993) or liquid-liquid extraction (LLE) (Borges, Freire, Martins, & Siqueira, 2009; Park, Pyo, Park, & Park, 2005). But, these techniques often require large sample volumes and use organic solvents as well as being time-consuming, which make them costly, difficult and tedious. In the recent years, economic, efficient miniaturized sample preparation methods have been developed, such as solid phase microextraction (SPME) (Alpendurada, 2000; Penalver, Pocurull, Borrull, & Marce, 1999) and liquid phase microextraction (LPME) (Psillakis & Kalogerakis, 2003; Rasmussen & Pedersen-Bjergaard, 2004). LPME is a miniaturized sample preparation method in which a few microliters of an organic solvent are used as a solvent (Liu & Dasgupta, 1995). Rezaee et al. (2006) developed a LPME method, specifically dispersive liquid-liquid microextraction (DLLME). In this method, a mixture of disperser and extraction solvents quickly disperses in an aqueous sample forming a cloudy solution. The cloudy solution indicates dispersion of the solvents in an aqueous solution with a large surface contact area. The analytes are extracted and enriched in the fine droplets of solvent, which are then separated by centrifugation (Rahnama Kozani, Assadi, Shemirani, Millani Hosseini, & Jamali, 2007). Lately, a new version of DLLME, namely elevated temperature-dispersive liquid-liquid microextraction (ET-DLLME), has been proposed (Farajzadeh, Afshar Mogaddam, & Gorbanpour, 2014). The difference with this method from traditional DLLME is the use of a pre-heated sample that disperses immediately on injection into the solvents. At a high temperature, solubility of the solvent in an aqueous solution is higher compared with an ambient or low temperature sample. After injection, the solution cools and forms more droplets of the extraction solvent leading to greater extraction efficiency.

The main goal of this study was application of the ET-DLLME method followed by GC determination for some OPP residues in an aqueous sample. Using a high volume of sample (50 mL) and a low volume of the disperser solvent (1.5 mL vs. 50 mL sample solution), high enrichment factors could be achieved. In addition, a relatively small volume of the extraction solvent was used (µL level vs. 50 mL sample solution). Different experimental conditions affecting the microextraction efficiency were examined and the selected pesticides (common pesticides used in Iran) determined in water and fruit juice samples.

2. Material and methods

2.1. Materials and reagents

All OPPs (dichlorvos, diazinon, malathion, chlorpyrifos, profenofos, and phosalone) with purities >98% were obtained from GYAH Corporation (Karaj, Iran). 1,1,2-Trichloroethane (1,1,2-TCE) (98%) and 1,1,2,2-tetrachloroethane (1,1,2,2-TCE) (97%) were from Janssen Chimica (Beerse, Belgium). 1,2-Dibromoethane (1,2-DBE) (>98%) was from Merck (Darmstadt, Germany). The tested disperser solvents, including HPLC-grade dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), and n-propanol and compounds such as sodium hydroxide, hydrochloric acid, and sodium chloride, were also obtained from Merck. Deionized water (Ghazn Company, Tabriz, Iran) was used for the preparation of aqueous solutions. Stock solutions of the OPPs at 1000 mg L\(^{-1}\) (each analyte) was prepared by dissolving appropriate amounts in acetone. The stock solution was diluted to obtain working solutions using deionized water. For system control, and calculation of enrichment factors and extraction recoveries, a standard solution was prepared in 1,2-DBE at 150 mg L\(^{-1}\) for each pesticide. This solution was injected directly into the system three times a day.

2.2. Instruments

A Shimadzu gas chromatograph GC-2014 (Shimadzu, Kyoto, Japan), equipped with a split/splitless injector adjusted at 300 °C in a splitless mode (sampling time 1 min) and a flame ionization detector (FID), was used in this study. Helium (Gulf Cryo, United Arab Emirates – purity of 99.999%) was used as the carrier gas at a constant linear velocity (30 cm s\(^{-1}\)). An OPTIMA delta-3 capillary column (30 m × 0.25 mm i.d., and the film thickness of 0.5 µm) (Macherey-Nagel, Germany) was used for separation of the target OPPs. Hydrogen was produced using a hydrogen generator (OPGU-1500S, Shimadzu, Japan) and FID was at a flow rate of 30 mL min\(^{-1}\). The column oven was programmed as follows: initially held at 50 °C for 1 min, then the temperature was raised to 300 °C at a rate of 15 °C min\(^{-1}\), and held at 300 °C for 2 min. The FID temperature was adjusted at 300 °C. An Agilent 7890A gas chromatograph equipped with a 5975C mass selective detector (Agilent Technologies, CA, USA) was used in gas chromatography–mass spectrometry (GC–MS) analysis. The system was equipped with a split/splitless injector operated at 300 °C in a splitless mode (sampling time 1 min). An HP-5 MS capillary column (30 m × 0.25 mm i.d., and the film thickness of 0.25 µm) (Hewlett-Packard, Santa Clara, USA) was used for separation of the OPPs in the GC–MS system. In the GC–MS and GC-FID systems, the oven temperature programmes were the same. The MS operational conditions were: ion source temperature: 250 °C, electron ionization (EI) at 70 eV; mass analyzer: quadrupole; mass range: m/z 55–350; transfer line temperature: 260 °C; acquisition rate: 20 Hz; and detector voltage: −1700 V. The commercial NIST library was used to confirm identify. A Metrohm pH meter model 654 (Herisau, Switzerland) was used to monitor pH. A ROTOFIX 32A centrifuge (Hettich, Germany) was also used throughout.

2.3. Samples for analysis

Samples, such as onion, and grape and apple juices were purchased from local vendors (Tabriz, Iran). The onions were cut into small pieces and 100 g was squeezed using a commercial food processor (Black & Decker, USA). The onion juice was diluted with deionized water at a ratio of 1:10. Two river water samples were collected from the Zarrineh and Simineh rivers (Miandoab, West Azerbaijan, Iran). The river waters were used without filtration or dilution. The apple and grape juice samples were diluted with deionized water at a ratio of 1:2 before analysis. All samples were stored in a refrigerator at 4 °C before analysis.

2.4. Sample preparation method

A 50 mL of each sample or standard solution containing NaCl (5%, w/v) was transferred into a 70-mL conical bottom glass test tube. The tube was placed in a water bath (at 80 °C) for 5 min
and 1.5 mL DMSO (disperser) and 104 μL 1,2-DBE (extractor) added rapidly using a 5-mL glass syringe to obtain a moderately turbid solution. The solution was allowed to cool to room temperature. The solution became more turbid as the solution cooled. Then, the cloudy solution was centrifuged at 1431 g for 4 min, which sediments ca. 20 ± 1 μL of 1,2-DBE at the bottom of the tube. Finally, 1 μL of 1,2-DBE was injected into the GC-FID.

2.5. Calculation of enrichment factor (EF) and extraction recovery (ER)

EF is determined by dividing the concentration of the analyte in the final organic phase (C_{sed}) by the concentration of the analyte (C_0) in the sample.

\[
EF = \frac{C_{sed}}{C_0}
\]

ER is calculated by comparing peak areas for the enriched analytes with peak areas of the target analytes which was obtained from direct injection of the prepared standard solution in 1,2-DBE.

\[
ER = \frac{n_{sed}}{n_0} \times 100 = \frac{C_{sed} \times V_{sed}}{C_0 \times V_{aq}} \times 100 = EF \times \left( \frac{V_{sed}}{V_{aq}} \right) \times 100
\]

where V_{sed} and V_{aq} are the final organic phase and aqueous sample volumes, respectively.

3. Optimization steps

In present work, an ET-DLLME-GC-FID method is proposed for the analysis of OPPs in different matrices. The initial objective was to optimize the microextraction method to obtain more EFs and ERs. Thus, some extraction conditions that might impact the performance of ET-DLLME method, including volume and type of extraction and dispersion solvents, ionic strength, pH and temperature, were examined in detail one variable at a time (OVAT), which ensures the variable responsible for any effect observed is clearly identified.

3.1. Optimization of extraction solvent kind

Choosing a good extraction solvent is most important for DLLME. Properties such as density, extraction capacity, solubility, good gas chromatographic behavior, and dispersion in the aqueous solution must be considered. Based on these criteria, and in view of this fact that the ET-DLLME method uses relatively high boiling point solvents for extraction, halogenated solvents including 1,2-DBE (b.p. 132 °C), 1,1,2-TCE (b.p. 113.8 °C), and 1,1,2,2-TCE (b.p. 146.5 °C) were investigated. To obtain a same volume of sediment, 110 μL of 1,2-DBE, 120 μL of 1,1,2-TCE and 140 μL of 1,1,2,2-TCE mixed with 2 mL DMF individually, and the mixtures used in the proposed method to determine the spiked concentration (25 ng mL⁻¹ of each analyte) of 50 mL deionized water at 75 °C. The ERs obtained are shown in Fig. 1. The results obtained showed that 1,2-DBE had the highest extraction efficiency for the target analytes compared with alternatives. Thus, 1,2-DBE was for subsequent steps.

3.2. Disperser solvent kind

Miscibility with sample solution and extraction solvent is an important parameter in a disperser. Accordingly, and because the method is performed at a high temperature, three high boiling point solvents including DMF (b.p. 153 °C), DMSO (b.p. 189 °C), and n-propanol (b.p. 97 °C) were tested. Since different dispersive solvents at a constant volume could alter the volume of the sediment, using a constant volume of the extraction solvent, the type of disperser and volume of 1,2-DBE were adjusted simultaneously to ensure a near constant volume (10 ± 1 μL). Our experiments showed that, when 2 mL of DMF, DMSO and n-propanol (containing 110, 117 and 125 μL of 1,2-DBE, respectively) were used, the sedimented phase volume was 10 ± 1 μL and DMSO was more effective (data not shown). Therefore, DMSO was chosen as the disperser solvent for subsequent experiments.

3.3. Optimization of 1,2-DBE volume

In microextraction, solvent volume is a critical parameter. Usually, the extraction solvent volume is as small as possible to obtain the highest EFs and reasonable ERs, and minimize contamination of the environment. The volume of extraction solvent must be sufficient that efficient ERs for the target analytes are obtainable and the volume of sedimented phase is enough for subsequent chromatographic analysis. To optimize the volume, various volumes of 1,2-DBE (117, 125, 130, 140, and 170 μL) were investigated. By increasing the volume of 1,2-DBE from 117 to 140 μL, the sedimented phase volume increased from 10 to 60 μL. The results obtained show that up to 130 μL of 1,2-DBE increased ERs but any further increased had no effect. Thus, 130 μL of 1,2-DBE was used as the optimum volume. In this case, volume of the sedimented phase increased to 20 ± 1 μL.

3.4. Disperser solvent volume optimization

The disperser solvent volume affects solubility and dispersion quality in the aqueous phase. For this reason, different DMSO volumes (disperser solvent) caused some changes in sedimented phase volume. To obtain the optimum volume, DMSO and 1,2-DBE were altered simultaneously to achieve a constant volume of the final organic phase. For this purpose, DMSO volumes were altered from 0.5 to 3.0 mL along with 100–155 μL of 1,2-DBE and the mixtures were subjected to disperser solvent volume optimization. In all cases, the sedimented phase volume was constant (20 ± 1 μL). The results showed that ERs increased rapidly up to 1.5 mL DMSO and then decreased gradually (data not shown). With small volumes of DMSO, the cloudy state was not well formed and
The aqueous phase temperature was studied in the range 23 (room temperature)–90 °C. Results shown in Fig. 2 reveal that analytical signals for the target analytes increased with increasing temperature from 23 to 80 °C, and then decreased. The variation in solubility and migration rates for the target analytes at different temperatures can affect the distribution coefficients of OPPs. Thus, the ERs obtained varied in the temperature range studied. It was noticeable that, after dispersion, the main function of the sample solution was in preserving ERs. During cooling, turbidity of the aqueous phase increased, which can be attributed to the production of more solvent droplets. Therefore, 80 °C was chosen for subsequent steps.

3.7. Optimization of solution pH

Sample pH was evaluated over the range of 2–12 using 1 M NaOH or HCl to adjust the value. The data obtained demonstrated that peak areas for the selected OPPs increased in the range 2–5, and then nearly constant up to pH 7 (data not shown). At pH ≥ 8, the peak areas decreased, which could be attributed to hydrolysis in strongly acidic or alkaline solutions. All the samples tested were in the range of 5.5–6.7, meaning pH adjustment was not required.

3.8. Centrifugation speed and time optimization

Centrifugation is an essential step to accumulate the extraction solvent in an ET-DLLME method. Centrifuge speed and time were examined in the ranges 2–7 min and 358–2236 g, respectively. Analytical signals improved with increasing time up to 4 min. Also, the ERs obtained increased speed, reaching a plateau after 1431 g. Therefore, 4 min and 1431 g were selected as optimum.

3.9. Analytical performance

Under optimized conditions, analytical features of the method were investigated. Some parameters, including relative standard deviation (RSD), correlation coefficient (r), linear range (LR), limit of quantification (LOQ), LOD, ER, and EF, were calculated and are summarized in Table 1. Calibration curves were constructed using standard OPPs solutions at nine different concentrations after extraction. The LOQ and LOD were defined as the concentrations giving a signal to noise ratio of 10- and 3-fold, respectively. The intra-day and inter-day precision of the method were assessed by replicate injections of a standard solution (10 ng mL⁻¹ each pesticide) in a day (n = 6) and four consecutive days, respectively. The results are listed in Table 1. Good linearity was observed with a correlation coefficient >0.994. The LODs and LOQs were in the

<table>
<thead>
<tr>
<th>Analyte</th>
<th>LOD (ng mL⁻¹)</th>
<th>LOQ (ng mL⁻¹)</th>
<th>LR (ng mL⁻¹)</th>
<th>r²</th>
<th>RSD (%)</th>
<th>EF ± SD</th>
<th>ER ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichlorvos</td>
<td>1.65</td>
<td>5.18</td>
<td>5.18–1000</td>
<td>0.995</td>
<td>3.2</td>
<td>1600 ± 48</td>
<td>64 ± 2</td>
</tr>
<tr>
<td>Diazinon</td>
<td>0.85</td>
<td>2.60</td>
<td>2.60–1000</td>
<td>0.998</td>
<td>4.4</td>
<td>2025 ± 81</td>
<td>81 ± 3</td>
</tr>
<tr>
<td>Malathion</td>
<td>1.54</td>
<td>5.90</td>
<td>5.90–1000</td>
<td>0.997</td>
<td>5.7</td>
<td>1875 ± 112</td>
<td>75 ± 4</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>0.82</td>
<td>3.20</td>
<td>3.20–1000</td>
<td>0.994</td>
<td>3.4</td>
<td>2075 ± 62</td>
<td>83 ± 2</td>
</tr>
<tr>
<td>Profenofos</td>
<td>0.89</td>
<td>3.10</td>
<td>3.10–1000</td>
<td>0.996</td>
<td>4.5</td>
<td>1800 ± 72</td>
<td>72 ± 3</td>
</tr>
<tr>
<td>Phosalone</td>
<td>2.72</td>
<td>7.36</td>
<td>7.36–1000</td>
<td>0.998</td>
<td>4.2</td>
<td>1750 ± 70</td>
<td>70 ± 3</td>
</tr>
</tbody>
</table>

Notes:
- a Limit of detection (S/N = 3).
- b Limit of quantification (S/N = 10).
- c Linear range.
- d Correlation coefficient.
- e Relative standard deviation (C = 10 ng mL⁻¹ of each pesticide) for intra-day (n = 6) and inter-days (n = 4).
- f Enrichment factor ± standard deviation (n = 3).
- g Extraction recovery ± standard deviation (n = 3).
ranges 0.82–2.72 and 2.60–7.36 ng mL\(^{-1}\), respectively. Good repeatability was obtained with the RSDs less than 5.7% for intra-day (\(n = 6\)) and 7.4% for inter-day (\(n = 4\)). High EFs in the range 1600–2075, and ERs in the range of 64–83% despite use of a high volume ratio of aqueous phase to organic phase (50/0.02 = 2500), were achieved. High EFs, low LOQs and LODs, and good repeatability are the principal benefits of the proposed procedure.

3.10. Real samples analysis

The performance of the method using several samples was assessed. Fig. 3I depicts the GC-FID chromatograms of blank, apple, grape, and onion juices, and two river water samples. In the chromatogram from apple juice, a peak (indicated by an arrow) eluted at the retention time associated with diazinon at a concentration of 29 ± 3 ng mL\(^{-1}\) (\(n = 3\)) can be observed. For subsequent confirmation, the apple juice was also analyzed by GC–MS (Fig. 3II). The presence of diazinon in the apple juice was verified by comparison of mass data from scan 2139 (retention time 18.70 min) with those of the target pesticide. To study any potential matrix effect, the samples were spiked with target OPPs at three concentrations (25, 50, and 100 ng mL\(^{-1}\) of each analyte) before analysis using the new method (\(n = 3\)). Mean relative recoveries, obtained from analytical signals for the selected OPPs in samples against the de-ionized water (with the similar concentrations), are tabulated in Table 2. The results showed that the sample matrices had no effect on the efficiency of the method. A relatively high matrix effect was observed with onion, apple and grape juices samples without dilution. Therefore, the onion juice was diluted 1:10 with de-ionized water to decreased matrix effect significantly. The grape and apple juices were diluted 1:2 as stated in Table 2.

3.11. Evaluation of the developed method with other presented methods

The performance of the method was compared with other reported methods used in the analysis of the OPPs, considering LOQ, LOD, EF, and RSD, as shown in Table 3. The RSDs for the method developed is comparable or better than other methods. LOD for the method is better than alternatives. It must be noted that, in some methods, two sample preparation steps or a high selective detection system, such as flame photometric detection

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**Table 2**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Mean relative recovery ± standard deviation ((n = 3))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onion juice</td>
</tr>
<tr>
<td>All samples were spiked with each analyte at a concentration of 25 ng mL(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Dichlorvos</td>
<td>96 ± 3</td>
</tr>
<tr>
<td>Diazinon</td>
<td>97 ± 2</td>
</tr>
<tr>
<td>Malathion</td>
<td>98 ± 1</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>99 ± 3</td>
</tr>
<tr>
<td>Profenofos</td>
<td>98 ± 3</td>
</tr>
<tr>
<td>Phosalone</td>
<td>94 ± 3</td>
</tr>
<tr>
<td>All samples were spiked with each analyte at a concentration of 50 ng mL(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Dichlorvos</td>
<td>96 ± 3</td>
</tr>
<tr>
<td>Diazinon</td>
<td>91 ± 3</td>
</tr>
<tr>
<td>Malathion</td>
<td>97 ± 3</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>89 ± 3</td>
</tr>
<tr>
<td>Profenofos</td>
<td>98 ± 3</td>
</tr>
<tr>
<td>Phosalone</td>
<td>99 ± 4</td>
</tr>
<tr>
<td>All samples were spiked with each analyte at a concentration of 100 ng mL(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Dichlorvos</td>
<td>97 ± 3</td>
</tr>
<tr>
<td>Diazinon</td>
<td>98 ± 3</td>
</tr>
<tr>
<td>Malathion</td>
<td>98 ± 3</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>98 ± 4</td>
</tr>
<tr>
<td>Profenofos</td>
<td>99 ± 3</td>
</tr>
<tr>
<td>Phosalone</td>
<td>99 ± 4</td>
</tr>
</tbody>
</table>

\(^a\) Diazinon content of the sample is subtracted.
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References


Table 3

Comparison of the presented method with the other methods used in preconcentration and determination of the target analytes.

<table>
<thead>
<tr>
<th>Method</th>
<th>Analytes</th>
<th>Sample</th>
<th>LR</th>
<th>LOD</th>
<th>RSD</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>UASE-DLLME-SFO-HPLC-UV&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Diazinon, Phosalone, Chlorpyrifos</td>
<td>Summer crops</td>
<td>5–500 (µg kg&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2 (µg kg&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.5</td>
<td>Pirsaheb, Fattahi, and Shamsipur (2013)</td>
</tr>
<tr>
<td>GCC × GC-FPD&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Dichlorvos, Malathion, Chlorpyrifos</td>
<td>Green vegetable, Rice and apple</td>
<td>5–1000 (µL&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.6 (µL&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>13</td>
<td>Liu, Mitrovski, Li, Li, and Marriott (2013)</td>
</tr>
<tr>
<td>SPME-GC-FPD&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Malathion, Diazinon</td>
<td>Aqueous sample</td>
<td>0.5–100 (µg L&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.28 (µg L&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.1</td>
<td>Yao et al. (2001)</td>
</tr>
<tr>
<td>CPE-GC-FPD&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Dichlorvos, Diazinon, Chlorpyrifos, Malathion</td>
<td>Fruit juice, Water sample</td>
<td>5–200 (µg kg&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1.5 (µg kg&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>4.56</td>
<td>Zhao et al. (2011)</td>
</tr>
<tr>
<td>DLLME-GC-FID&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Diazinon</td>
<td>Water sample</td>
<td>10–100,000 (µg L&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>3.0 (µg L&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>6</td>
<td>Farajzadeh, Seyedi, Safi Shalamzari, and Bamorowat (2009)</td>
</tr>
<tr>
<td>ET-DLLME-GC-FID&lt;sup&gt;g&lt;/sup&gt;</td>
<td>Six OPPs</td>
<td>Aqueous sample</td>
<td>3–1000 (ng mL&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;g&lt;/sup&gt;</td>
<td>0.82–2.72 (ng mL&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;g&lt;/sup&gt;</td>
<td>3.2–5.7</td>
<td>This method</td>
</tr>
</tbody>
</table>

<sup>a</sup> Linear range.
<sup>b</sup> Limit of detection.
<sup>c</sup> Relative standard deviation.
<sup>d</sup> Ultrasonic-assisted solvent extraction-dispersive liquid-liquid microextraction-solidification of floating organic drop-high performance liquid chromatography-ultraviolet detector.
<sup>e</sup> Comprehensive two-dimensional gas chromatography-flame photometric detector.
<sup>f</sup> Solid-phase microextraction-gas chromatography-flame photometric detector.
<sup>g</sup> Cloud point extraction-gas chromatography-flame photometric detector.

(FPD), were used. Another advantage of the method developed was EFs near to the ideal or theoretical values (50/0.02 = 2500). Based on these considerations, the proposed method proved to be a sensitive, rapid, reliable, simple and efficient for the extraction and pre-concentration of the selected OPPs from aqueous samples.

4. Concluding remark

In the present work, an ET-DLLME method was proposed for the preparation of some OPPs prior to their analysis with GC-FID. The results obtained showed that the method exhibited many merits, such as low LODs, high ERs and EFs, and good repeatability. Finally, the proposed method was applied to the extraction and analysis of selected OPPs in liquid samples, and diazinon was determined in apple juice at ng mL<sup>−1</sup> levels.

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