Ultrasound-assisted temperature-controlled ionic liquid dispersive liquid-phase microextraction combined with reversed-phase liquid chromatography for determination of organophosphorus pesticides in water samples

A rapid and sensitive ultrasound-assisted temperature-controlled ionic liquid (IL) dispersive liquid-phase microextraction (UTILDLPME) combined with reversed-phase liquid chromatography-ultraviolet (RPLC-UV) was developed for the determination of five organophosphorus pesticides (OPPs; azinphos-methyl, chloropyriphos, parathion-methyl, diazinon, and phosalone) in water samples. Parameters including IL type, IL volume, ionic strength, sonication time, heating/cooling temperature, centrifugal time, and speed were investigated. The extraction procedure was induced by the formation of cloudy solution, which was composed of 75 μL of 1-butyl-3-methylimidazolium hexafluorophosphate ([C4MIM]PF6) dispersed entirely into 5 mL sample solution with the assistance of ultrasound for 3 min and temperature at 40°C. Under optimal conditions, linearity of the five OPPs was obtained in the range of 0.09–200 ng/mL with correlation coefficients of 0.998 or more. Limits of detection and limits of quantitation ranged from 0.01 to 0.1 ng/mL and from 0.05 to 0.4 ng/mL, respectively. Compared with conventional microextraction techniques, the proposed UTILDLPME exhibited the highest extraction efficiency ranging between 90 and 98% for targeted OPPs. Furthermore, the proposed UTILDLPME/RPLC was successfully applied to different water samples (tap, well, and lake water) showing relative recoveries ranging from 96.9 to 103.2%. Therefore, UTILDLPME/RPLC-UV could be a simple, rapid, sensitive, and efficient routine technique for determination of OPPs in water.

Keywords: HPLC / Ionic liquids / Microextraction / Organophosphorus pesticides / Ultrasound DOI 10.1002/elps.201600107

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1 Introduction

Hydrophobic ionic liquids (ILs) have gained widespread recognition as novel ecofriendly extraction solvents instead of water-immiscible toxic organic solvents in dispersive liquid-phase microextraction (DLPME) [1–4]. Among other “green” features, ILs are relatively thermally stable and display limited potential to contaminate the atmosphere, especially when compared with traditional volatile organic solvents [5–8]. ILs can be easily prepared from relatively inexpensive materials and tuned by combination of different anions and cations for task-specific extraction of analytes. The most commonly employed ILs in IL dispersive-liquid-phase microextraction (ILDLPME) are 1-alkyl-3-methyl-imidazolium hexafluorophosphate [CnMIM]PF6 that could be formulated by

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Abbreviations: DLPME, dispersive liquid-phase microextraction; IL, ionic liquid; ILDLPME, IL dispersive liquid-phase microextraction; OPPs, organophosphorus pesticides; UTILDLPME, ultrasound-assisted temperature-controlled ILDLPME

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changing the number of carbons from two to eight in the alkyl chain [9]. It was obvious that with the increase of alkyl chain length, the extraction performance of ILs for analytes was improved [10]. This could be attributed to the lower solubility of ILs in the aqueous sample when longer alkyl chain was substituted at the imidazole ring. Besides classical ILDLPME with organic solvents as dispersing agents, different alternatives were developed to obtain a dispersion of the extraction solvent into sample solutions [10]. Thus, increase of temperature or application of ultrasound energy to sample solutions was employed as dispersant tools in microextraction procedures [11, 12]; despite emerging ultrasound and temperature control in ILDLPME technique was developed in a few reports [13–15].

Recently, ultrasound-assisted temperature-controlled IL dispersive liquid-phase microextraction (UTILDLPME) has become an attractive alternative for sample preparation because of its high extraction efficiency, simplicity, speed, and low cost [15]. In this application, ultrasound irradiation concurrently with the heating temperature favors the dispersion of IL into the aqueous phase, whereas, further cooling of the solution requires facilitating the formation of the cloudy microdroplet state (emulsification) and speeds up mass transfer between the two immiscible phases; thereby, increasing the extraction yield and reducing the equilibrium time [14].

Organophosphorus pesticides (OPPs) are extensively used in agricultural field in order to increase its production due to their comparably low price and adequate ability to control pests, diseases, and weeds. However, the increased use of OPPs has resulted in persisting residues in environmental matrices. They may leach from soil to the ground water or surface water, which is considered a high risk to the animal and human health [16–19]. LC and GC have been the most generally used techniques in determination of pesticides due to its high selectivity and sensitivity. However, pesticides in water samples are not directly analyzed with chromatography due to their low concentrations and the complexity of the sample matrix. In general, trace determination of pesticides in samples usually requires a sample preparation step prior to chromatographic analysis. The primary pretreatment methods for OPPs in water samples are SPE [20], dispersive liquid-phase microextraction [21, 22], and single-drop microextraction [23]. However, these methods are labor-intensive, time-consuming, or deleterious in terms of organic solvents. Therefore, a simpler, more rapid, and more environment friendly liquid-phase microextraction technique is highly needed. Furthermore, the combination of ILDLPME with GC is not suitable due to the absence of vapor pressure, which prevents evaporation in typical vaporizing inlets for GC. This can result in contamination of the inlet, unstable chromatographic baselines, and possibly unstable column gas-flow rates [1]. For this reason, it is superior to combine ILDLPME with HPLC having sufficient organic modifier in the mobile phase to dissolve hydrophobic ILs.

Thus, the main objective of this study was, for the first time, to develop rapid, ecofriendly, sensitive, and efficient extraction approach by using UTILDLPME combined with RPLC for determination of five OPPs (azinphos-methyl, chloropyriphos, parathion-methyl, diazinon, and phosalone) in different water samples. In addition, it is a trial to enlarge the applications of commercially available ILs such as [C4MIM]PF6 in liquid-phase microextraction. Some parameters related with UTILDLPME such as type and volume of IL, ionic strength, sonication time, temperature, and extraction time were optimized.

2 Materials and methods

2.1 Chemicals and solutions

Chloropyriphos, Parathion-methyl, Azinphos-methyl, Diazinon, and Phosalone were purchased from Riedel-dehaën (Germany). 1-Butyl-3-methylimidazolium hexafluorophosphate [C4MIM]PF6, 1-hexyl-3-methylimidazolium hexafluorophosphate [C6MIM]PF6, and 1-octyl-3-methylimidazolium hexafluorophosphate [C8MIM]PF6 were purchased from Jingchun Chemical Reagent (China). Methanol, dichloromethane, ACN, and cyclohexane were purchased from Aldrich (Germany). Unless otherwise specified, the purities of all reagents were $\geq 99.7\%$ and used without further purification. Ultra-pure water produced by an ELGA model CLXXXUV2M (UK) was used for the preparation of solutions and mobile phases.

Standard stock solutions of 1000 $\mu$g/mL of each azinphos-methyl, parathion-methyl, and chloropyriphos were accurately prepared in 10 mL methanol. As well, stock solutions of 1000 $\mu$g/mL of each diazinon and phosalone were prepared in 10 mL ACN. All solutions were stored in PTFE-sealed screw-cap bottles at 4°C prior to use. Working mixture solutions were daily prepared by the appropriate dilution of the stock solutions with the appropriate organic solvent.

2.2 Instrumentation

Chromatographic separations were carried out with a PerkinElmer series 200 LC binary solvent delivery system (San Diego, Canada) with a Rheodyne injection valve (Model 7725(i)), a series 200 UV/Vis variable wavelength detector and series 200 vacuum degasser. Data were collected by TotalChrom™ chromatography data handling system. The optimum chromatographic separation was achieved in a short period with a binary mobile phase under isocratic conditions. The optimal RPLC conditions for the determination of targeted OPPs are summarized in Table 1. The first RPLC method composed of mobile phase containing 15% v/v water and 85% v/v methanol and the SupelcoC18 stationary phase for the separation of azinphos methyl, parathion methyl, and chloropyriphos. Moreover, 5% water and 95% ACN mobile phase used for the separation of diazinon and phosalone on a fused core pentafluorophenylpropyl stationary phase (Discovery™ HS F5 column). The pentafluorophenylpropyl...
column provides a reversed-phase packing with electron-deficient phenyl rings because of electronegative fluorines. This phase retains compounds by forming π–π interaction, possible steric interactions with bonded phase in addition to polar interactions.

2.3 Extraction procedure

The effective parameters of UTILDLPME for the extraction of five OPPs from different water samples were investigated. The optimal extraction procedure was achieved by taking a 5 mL water sample containing OPPs in a conical test tube followed by adding 75 μL of [C4MIM]PF$_6$. The mixture was then sonicated for 3 min at 30% amplitude concurrently with heating at 40°C. After that, the mixture was immediately cooled down to 3°C for 2 min and the IL droplet was settled at the bottom of the conical tube by centrifugation at 1700 × g for 2 min. The upper aqueous phase was removed with a Pasteur pipette and the sediment phase was withdrawn by a microsyringe. The IL extract was viscous to be injected directly into the HPLC system, thus it was diluted to 100 μL with methanol. The mixture was filtered through 0.22 μm nylon filters to remove any particles prior to HPLC measurement leading to prolonging the injector and column life [24]. Finally, 10 μL of resulting solution was injected into the HPLC system.

2.4 Procedure for water samples

Three tap water samples from three different districts in Jeddah city, Saudi Arabia (Tap 1 from Algama, Tap 2 from Alnaseem, and Tap 3 from Guaziah), one well water located in Taif city, Saudi Arabia, and one lake water located in Elkhorma city, Saudi Arabia, were tested as real samples. They were filtered through a 0.45 μm membrane filter (Scharlau, Barcelona, Spain) to remove any particulate matters and maintained in a refrigerator at 4°C until analysis. After that, 5 mL of solution was subjected to the UTILDLPME procedure as described in Section 2.3. For recovery determinations, water samples were spiked with a mixture of analytes at different concentration levels and were analyzed by the proposed UTILDLPME/RPLC-UV methods.

3 Results and discussion

3.1 Optimization of UTILDLPME

In order to obtain the maximal extraction efficiency of OPPs using UTILDLPME, several parameters that may influence the extraction process such as type of IL, volume of IL, ultrasonic time, temperature, centrifuging speed, and centrifuging time were investigated.

3.1.1 Type and volume of IL

The selection of an appropriate extraction solvent is extremely important for the LPME process. The alkyl chain length on the imidazolium ring of ILs has significant influence on its physical and chemical properties, such as density, viscosity, and extraction performance [25]. Therefore, three ILs [C4MIM]PF$_6$, [C6MIM]PF$_6$, and [C8MIM]PF$_6$ were studied and their recoveries for OPPs were compared as shown in Fig. 1. In general, it was found that increasing alkyl chain length from butyl to octyl decreased the extraction efficiency of analytes [25]. This could be attributed to raising of IL viscosity by increasing the length of alkyl side chain, which subsequently may hinder the dispersing of IL in the water phase. The order based on viscosity in water of the three ILs is [C8MIM]PF$_6$ (710 Pa/s), [C6MIM]PF$_6$ (560 Pa/s), and [C4MIM]PF$_6$ (312 Pa/s). Therefore, the dispersed droplets of [C8MIM]PF$_6$ can be adequately gathered and a cloudy emulsion can be formed more easily. However, withdrawing and transferring the IL phase by the microsyringe from the water phase was difficult because of its high viscosity. However, withdrawing and transferring the [C4MIM]PF$_6$ is more easier. In addition, the synergic effect of ultrasound and heating temperature followed by cooling facilitates the dispersion and emulsification of [C4MIM]PF$_6$. Furthermore, the [C4MIM]PF$_6$ peak did not interfere with the targeted OPPs peaks under the selected RPLC conditions, i.e. no effects attributable to the [C4MIM]PF$_6$ were observed on peak resolution, elution order, and elution time. Therefore, the use of UTILDLPME enlarges the application of commercially available [C4MIM]PF$_6$ as efficient extraction solvent.

The volume of extraction solvent is a crucial parameter that would have an important impact on the extraction efficiency of analytes. Therefore, the targeted OPPs were
subjected to UTILDLPME procedures included different volumes of [C4MIM]PF$_6$ ranging from 10 to 100 µL. The results are shown in (Supporting Information 1). The extraction recoveries increased with the increase of volume of IL from 10 to 75 µL, and decreased >75 µL. Therefore, 75 µL of [C4MIM]PF$_6$ was selected for further studies of OPPs. In these studies, the extraction recovery percent (R%) was calculated from the equation [25]:

$$R\% = \frac{C_{sed} \times V_{sed}}{C_0 \times V_{aq}} \times 100$$

where $R\%$, $C_{sed}$, and $C_0$ are the extraction recovery, the analyte concentration in the sediment, and the initial analyte concentration in the aqueous samples, respectively. $C_{sed}$ was calculated from the calibration graph. $V_{sed}$ and $V_{aq}$ are the volume of the sediment phase and the volume of the aqueous sample, respectively.

### 3.1.2 Ultrasound-assisted dispersion of IL

Ultrasound as a key procedure in UTILDLPME can accelerate the formation of fine dispersive mixture and result in higher recoveries. Efficient ultrasonication allows formation of a suitable suspension of IL in the sample solution without addition of a disperser organic solvent. The effect of ultrasonic agitation time on the dispersion of IL in aqueous phase was investigated in the range of 1–5 min (Supporting Information 2). It was found that the extraction efficiency was increased up to 3 min and then decreased after the extraction equilibrium was achieved. After IL was dispersed by ultrasonic agitation to form vesicles, the surface area between the extraction solvent [C4MIM]PF$_6$ vesicle and the aqueous phase is large. Thus, the mass transfer of the analytes from aqueous phase to extraction phase was fast. The main reason for the reduction of recoveries >3.0 min is most likely the volatilization loss of the OPPs in the extension of ultrasonic time. Therefore, 3 min was chosen as the optimal time for the ultrasonic agitation extraction procedure. Energy provided by ultrasound is needed to release the OPPs from the matrix. However, excessive energy may also accelerate the volatilization of OPPs and generate a great number of cavitation bubbles in the solution, which may dampen the passage of sound energy through the liquid. Therefore, different amplitude values were evaluated starting at the lowest values allowed by the system. The results indicated that extraction recovery increased with increasing amplitude from 5 to 30% and remained constant for higher amplitude values in most cases. The optimum extraction efficiency was obtained when 30% amplitude was utilized.

Furthermore, heating temperature could be considered as an adjunct driving force besides ultrasonication for the dispersion of ILs into an aqueous solution. It can also increase the contact area between [C4MIM]PF$_6$ and water, and affect the mass transfer rates of analytes. Conversely under lower temperatures, [C4MIM]PF$_6$ is not easily dispersed into the sample solution. Therefore, the effect of extraction temperature on the extraction recovery of OPPs was examined. The extraction processes were conducted in the range from 20 to 60°C for 3 min (Supporting Information 3). Results indicated that the extraction recovery increased from 20 to 40°C. Thereafter, the recoveries decreased with the further increase in temperature probably because of the loss of OPPs and sediment phase for the volatilization and IL larger solubility, respectively. Consequently, 40°C was chosen as the optimal heating temperature for UTILDLPME. After completion of analytes transfer into IL phase, the cooling may have an influence on the emulsification phenomenon of IL, i.e., cooling the IL dispersed in the sample solution prior to the sedimentation step favors the recovery of a larger volume of IL due to the decreased solubility. The effect of the cooling temperature was studied over the temperature range between 0 and 10°C for 2 min (Supporting Information 4). Results
indicated that the extraction recovery was increased down to 3°C, which was chosen for further experiments.

3.1.3 Effect of sample pH and ionic strength

The sample pH is another parameter that might affect the extraction efficiency of the five OPPs [26]. However, in the current work, it was observed that the adequate separation of droplet-phase contained analytes was obtained in a neutral medium around pHs 6–7, which is almost equal to pH of water samples; so all experiments were used without pH adjustment [26]. Furthermore, the influence of the ionic strength of the solution was evaluated by adding different amounts of sodium chloride (0–10%) to the sample solution. The results showed that the addition of salt decreased the extraction efficiencies of the target analytes. The addition of salt may enhance the solubility of IL in water, which may also decrease extraction efficiency. In this study, salt was not added in further experiments.

3.1.4 Effect of centrifugal rotational speed and time

In the UTILDLPME process, centrifugation plays an important role in the separation procedure [27]. The IL settles in the conical tube bottom during this process. The effect of centrifugal rotational speed on the extraction efficiency of the five target analytes was investigated in the range of 500–2000 × g. When the centrifugal rotational speed was set at 1700 × g, the maximum extraction efficiency was attained. Furthermore, centrifugation time affects the size of the settled phase and the concentration of analyte in the extraction phase. The effect of the centrifugation time on the extraction efficiency was investigated in the range of 0.5–5 min. Similar maximal recoveries were achieved using centrifugation times between 2 and 5 min at rotation speed 1700 × g. Thus, the lower value (2 min) was selected to speed up the sample preparation.

3.2 Comparison of UTILDLPME with conventional ILDLPME and DLPME

In the present work, for comparison, ILDLPME and DLPME were also developed for the extraction of targeted OPPs. In ILDLPME procedure, a solution of ACN containing [C4MIM]PF₆ was quickly introduced to the sample so-

3.3 Performance of the analytical procedures

Using a series of mixed analyte standard solutions spiked in water samples under the optimal extraction conditions, the developed UTILDLPME/RPLC methods were evaluated using the concentration linearity, the LOD, the LOQ, precision, and accuracy [28]. The obtained chromatographic features for the determination of azinphos-methyl, chloropyriphos, parathion-methyl, diazinon, and phosalone are presented in Table 2. The figures of merit of proposed methods for the determination of targeted OPPs are summarized in Table 3. Linearity observed in the range of 0.09–300 ng/mL for all OPPs with correlation coefficients (r) ranged from 0.9985 to 0.9999. The precision of the method was examined based on the triplicates of the three concentration levels of 10, 100, and 200 ng/mL. Intraday precision was measured on the same day, but interday precision was measured on three consecutive days. The recoveries for the spiked water samples were calculated with each sample running three times at three different concentration levels. The average extraction recoveries for analytes were found in the range of 86.2–108.1% and the RSDs varied from 1.75 to 3.71% (n = 9). The LOD and the LOQ were obtained by determining the minimum amount of each analyte required to give a S/N of 3 and 10. The obtained values of LODs, which varied between 0.01 and 0.10 ng/mL,

| Analytes         | tᵢ, min | Nᵢ | Rᵢ | Aᵢ | Kᵢ | αᵢ |
|------------------|---------|----|----|----|----|----|
| RPLC(1)          |         |    |    |    |    |    |
| Azinphos-methyl  | 2.1     | 1790 | —  | 1.2 | 0.6 | —  |
| Parathion-methyl | 2.4     | 2197 | 2.5 | 1.1 | 0.9 | 1.5 |
| Chloropyriphos   | 2.9     | 3668 | 4.0 | 1.0 | 1.2 | 1.3 |
| RPLC(2)          |         |    |    |    |    |    |
| Phosalone        | 5.0     | 4042 | 1.0 | 0.3 | —  | —  |
| Diazinon         | 5.2     | 4155 | 1.7 | 1.1 | 0.4 | 1.3 |

a) tᵢ: retention time.
b) Number of theoretical plates: N = 5.545(tᵢ/W₀₁₀₀)².
c) Resolution for two adjacent peaks: Rᵢ = 2(Δtᵢ – trᵢ)/(W₁ + W₂).
d) Asymmetry factor: Aᵢ = b/a, where a and b are measured at 10% of the peak height.
e) Retention factor: K = tᵢ/tₒᵢ.f)
 Selectivity: α = tᵢ⁻ / tₒ₀⁻.
Table 3. The performance characteristics of the proposed UTILDLPME/RPLC methods

| Analytes           | Linearity range, ng/mL | LODs, ng/mL | LOQs, ng/mL | RSD | Recovery<sup>a</sup>, % |
|--------------------|------------------------|-------------|-------------|-----|-------------------------|
|                    |                        |             |             |     |                         |
|                    |                        | Intraday, n = 3 | Interday, n = 9 |
| RPLC(1)            |                        |             |             |     |                         |
| Azinphos-methyl    | 0.40–200.00            | 0.09        | 0.32        | 0.04 | 1.75                    |
|                    |                        |             |             |     | 96.4–108.1              |
| Parathion-methyl   | 0.40–200.00            | 0.10        | 0.40        | 0.03 | 2.15                    |
|                    |                        |             |             |     | 86.2–98.0               |
| Chloropyriphos     | 0.40–300.00            | 0.10        | 0.33        | 0.03 | 1.85                    |
|                    |                        |             |             |     | 93.6–101.2              |
| RPLC(2)            |                        |             |             |     |                         |
| Phosalone          | 0.09–200.00            | 0.01        | 0.05        | 0.17 | 2.52                    |
|                    |                        |             |             |     | 89.4–101.5              |
| Diazinon           | 0.20–200.00            | 0.03        | 0.10        | 0.32 | 3.71                    |
|                    |                        |             |             |     | 99.3–103.0              |

<sup>a</sup> Recovery was calculated at three concentration levels of 10, 100, and 200 ng/mL.

were lower than or equal that given by the European Union allowing a maximum concentration of 0.1 ng/mL of each individual pesticide in drinking water [29]. These results indicated that the proposed UTILDLPME combined with RPLC approaches were reliable and sensitive procedures to determine OPPs at trace levels. Under the optimal UTILDLPME/RPLC conditions, chromatograms of OPPs are shown in Fig. 2.

3.4 Application

In order to evaluate the applicability of the proposed methods, the extraction and determination of azinphos-methyl, parathion-methyl, chloropyriphos, phosalone, and diazinon were performed in tap water, well water, and lake water samples. Samples were treated by UTILDLPME under optimal extraction conditions followed by RPLC-UV determination. The water samples were analyzed and the subsequent results are shown in Supporting Information 5. Data indicated adequate recovery values in all instances ranging from 96.9 to 103.2% that confirmed the validity of the proposed methods. These results proved that the matrices of real samples had little effects on the proposed UTILDLPME method for extraction of OPPs from water samples. Further confirmation for the selectivity of the current UTILDLPME/RPLC-UV was performed by repeating the measurements of four OPPs (azinphos-methyl, parathion-methyl, chloropyriphos, and diazinon) in the same water samples using ASTM D5175 GC/MS standard methodology as described in Supporting Information 6. The phosalone OPP was not measured by the standard method. The obtained results for the studied OPPs by the standard method are very close to those obtained by the proposed method that also confirm the validity of the present work for application to real water matrices.

4 Concluding remarks

In the present work, the synergic effect of ultrasound and temperature control as dispersant tools for [C4MIM][PF<sub>6</sub>] IL microextraction solvent in water was first used for the extraction and determination of five OPPs by combination with RPLC-UV. The proposed technique was compared with other techniques as shown in Table 4. It can be seen that the present
Table 4. Comparison of the present method with other hitherto published extraction techniques combined with HPLC for the determination of OPPs in water samples

| Extraction technique | Analytes                        | Linearity, ng/mL | LOD, ng/mL | RSD%, n = 9 | Reference |
|----------------------|--------------------------------|------------------|------------|-------------|-----------|
| IPA-LPE              | Chloropyrifos, diazinon, fenitrothion, methidathion, metsulfuron-methyl, nicosulfuron, prosulfuron, and rimsulfuron | 1.8–450.0 | 0.5–3.0 | —          | [30]      |
| SDME                 | Isoxcarbophos                   | 2.0–1000.0 | 0.45      | 4.4–5.8    | [23]      |
| SPE                  | Paraoxon, methyl-parathion, ethyl-parathion, Guthion, and fenitrothion | —         | 26.0–57.0 | <3.55      | [20]      |
| UAEME                | Isoxcarbophos, phosmet, parathion-parathion-methyl, fenitrothion, fonofos, and phoxim | 1.0–200.0 | 0.1–0.3 | 3.3–5.6    | [12]      |
| DLPME-SFO            | Triazophos, parathion, diazinon, phoxim, and parathion-parathion-methyl | 1.0–200.0 | 0.1–0.3 | 4.4–6.3    | [21]      |
| DLPME                | Fenitrothion, diazinon, and ethion | 10.0–4000.0 | 2.0–3.0 | 2.2–4.1    | [22]      |
| ILDLPME              | Fenitrothion, parathion, fenthion, and phoxim | 5.0–1000.0 | 0.01–0.05 | 1.1–2.7    | [27]      |
| ILDLPME              | Parathion, phoxim, phorate, and chlorpyrifos | 10.2–1089.0 | 0.1–5.0 | <4.7       | [26]      |
| UTILDLPME            | Azinphos-methyl, chloropyrifos, parathion-parathion-methyl, diazinon, and phoxaline | 0.09–200.0 | 0.01–0.1 | 1.8–3.7    | Current method |

DLPME-SFO: dispersive liquid-phase microextraction based on solidification of floating organic droplet; IPA-LPE: ion-pair assisted liquid-phase extraction; UAEME: ultrasound-assisted emulsification microextraction.

The technique provides LODs (LODs = 0.1–1.0) comparable to, or better than other techniques with linearity between 0.09 and 200.0 ng/mL. Moreover, precision of the proposed methodology, in terms of RSD (1.8–3.7%, n = 9), was found to be comparable to, or better than other methodologies. Besides, the current extraction procedure used ultrasound and heating temperature to obtain a dispersion of the IL extraction solvent into sample solution instead of using traditional volatile organic solvents (e.g., methanol) in classical ILDLPME technique [26, 27]. Therefore, the possibility of obtaining more reproducible results with high extraction efficiency (90–98%) was achieved since evaporation of volatile organic extractant was not required and further a directly analyzable extract with RPLC-UV in a short analysis time (extraction time is 3 min followed by about 6 min RPLC analysis) was performed. The accuracy of proposed method, in terms of recovery, showed adequate values in the range of 96.9–103.2%. These results indicate that UTILDLPME-HPLC was a simple, environmentally friendly, rapid, sensitive, and selective, with the additional advantages of using low cost and widely spread instrumentation that could be used for the routine analysis of OPPs in water samples.

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5 References

[1] Poole, C. F., Lenca, N., Trends Anal. Chem. 2015, 71, 144–156.
[2] Han, D., Tang, B., Lee, Y. R., Row, K. H., J. Sep. Sci. 2012, 35, 2949–2961.
[3] Martinis, E. M., Berton, P., Monasterio, R. P., Wuilloud, R. G., Trends Anal. Chem. 2010, 29, 1184–1201.
[4] Stanisz, E., Werner, J., Zgola-Grzeškiwiaik, A., Trends Anal. Chem. 2014, 61, 54–66.
[5] Abd El-Hady, D., Albishri, H. M., Rengarajan, R., Wätzig, H., Electrophoresis 2014, 35, 1956–1964.
[6] Abd El-Hady, D., Albishri, H. M., J. Chromatogr. B 2014, 969, 224–229.
[7] Albishri, H. M., Abd El-Hady, D., Talanta 2014, 118, 129–136.
[8] Abd El-Hady, D., Albishri, H. M., Talanta 2015, 139, 150–158.
[9] Zaijun, L., Xiulan, S., Junkang, L., in: Kokorin, A. (Ed.), Ionic Liquids: Applications and Perspectives, InTech, Croatia 2011, 153–207.
[10] Trujillo-Rodriguez, M. J., Rocio-Bautista, P., Pino, V., Afozon, A. M., Trends Anal. Chem. 2013, 51, 87–106.
[11] Aguiler-Herrador, E., Lucena, R., Cardenas, S., Valcarcel, M., Trends Anal. Chem. 2010, 29, 602–616.
[12] Zhang, J., Gao, H., Peng, B., Li, S., Zhou, Z., J. Chromatogr. A 2011, 1218, 6621–6629.
[13] Berton, P., Martinis, E. M., Martinez, L. D., Wuilloud, R. G., Anal. Chim. Acta 2012, 713, 56–62.
[14] Yan, Y., Chen, X., Hu, S., Tian, J., Bai, X., J. Chromatogr. Sci. 2014, 52, 218–225.
[15] Dong, W., Yu, S., Deng, Y., Pan, T., J. Chromatogr. B 2016, 1008, 45–49.
[16] Ahmad, W., Al-Sibaai, A. A., Bashammakh, A. S., Alwael, H., El-Shahawi, M. S., Trends Anal. Chem. 2015, 72, 181–192.
[17] Mahour, R., Khan, M. F., Forbes, S., Perez-Estrada, L. A., Water Environ. Res. 2014, 86, 1545–1578.
[18] Liang, H. C., Razaviarani, V., Buchanan, I., *Water Environ. Res.* 2013, 85, 1601–1645.

[19] Al Naggar, Y., Codling, G., Vogt, A., Naiem, E., Mona, M., Seif, A., Giesy, J. P., *Ecotoxicol. Environ. Saf.* 2015, 114, 1–8.

[20] Martinez, R. C., Gonzalo, E. R., Moran, M. J. A., Mendez, J. H., *J. Chromatogr. A* 1992, 607, 37–45.

[21] Wu, C., Liu, H., Liu, W., Wu, Q., Wang, C., Wang, Z., *Anal. Bioanal. Chem.* 2010, 397, 2543–2549.

[22] Farajzadeh, M. A., Bahram, M., Vardast, M. R., Bamorowat, M., *Microchim. Acta* 2011, 172, 465–470.

[23] Wang, X., Cheng, J., Wang, X., Wu, M., Cheng, M., *Analyst* 2012, 137, 5339–5345.

[24] Abd El-Hady, D., Albishri, H. M., *J. Liq. Chromatogr. Relat. Technol.* 2014, 37, 2681–2697.

[25] Huang, K.-J., Jin, C.-X., Song, S.-L., Wei, C.-Y., Liu, Y.-M., Li, J., *J. Chromatogr. B* 2011, 879, 579–584.

[26] He, L., Luo, X., Xie, H., Wang, C., Jiang, X., Lu, K., *Anal. Chim. Acta* 2009, 655, 52–59.

[27] He, L., Luo, X., Jiang, X., Qu, L., *J. Chromatogr. A* 2010, 1217, 5013–5020.

[28] ICH Harmonized Tripartite Guideline, Validation of Analytical Procedures: Text and Methodology, Q2(R1), Current Step 4 Version, Parent Guidelines on Methodology, dated November 6 1996, incorporated in November 2005, http://www.ich.org/LOB/media/MEDIA417.pdf.

[29] Drinking Water Guideline, 98/83/EEC, European Union, Brussels, 1998.

[30] Gure, A., Megersa, N., Retta, N., *Anal. Methods* 2014, 6, 4633–4642.