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Research Article

Sequential dispersive liquid–liquid microextraction for the determination of aryloxyphenoxy-propionate herbicides in water

A novel dispersive liquid–liquid microextraction (DLLME) method followed by HPLC analysis, termed sequential DLLME, was developed for the preconcentration and determination of aryloxyphenoxy-propionate herbicides (i.e. haloxyfop-R-methyl, cyhalofop-butyl, fenoxaprop-P-ethyl, and fluazifop-P-butyl) in aqueous samples. The method is based on the combination of ultrasound-assisted DLLME with in situ ionic liquid (IL) DLLME into one extraction procedure and achieved better performance than widely used DLLME procedures. Chlorobenzene was used as the extraction solvent during the first extraction. Hydrophilic IL 1-octyl-3-methylimidazolium chloride was used as a dispersive solvent during the first extraction and as an extraction solvent during the second extraction after an in situ chloride exchange by bis[(trifluoromethane)sulfonyl]imide. Several experimental parameters affecting the extraction efficiency were studied and optimized with the design of experiments using MINITAB® 16 software. Under the optimized conditions, the extractions resulted in analyte recoveries of 78–91%. The correlation coefficients of the calibration curves ranged from 0.9994 to 0.9997 at concentrations of 10–300, 15–300, and 20–300 μg L^{-1}. The relative SDs ($n = 5$) ranged from 2.9 to 5.4%. The LODs for the four herbicides were between 1.50 and 6.12 μg L^{-1}.

Keywords: Aryloxyphenoxy-propionate herbicides / In situ halide exchange reaction / Response surface methodology / Sequential dispersive liquid–liquid microextraction / Ultrasound
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1 Introduction

In recent years, there has been a movement toward simplified and miniaturized methods for sample pretreatment. Different microextraction techniques have been explored as alternatives to conventional extraction procedures. Solid-phase microextraction [1], stir bar sorptive extraction [2], and liquid-phase microextraction (LPME) have been introduced and applied to the preconcentration of different analytes. Single-drop microextraction [3,4] and hollow fiber LPME (HF LPME) [5,6] were developed early on as LPME techniques, and they have been applied to the preconcentration and determination of various pesticides [7–11]. Other LPME methods, such as solidification of a floating organic drop [12] and cloud point extraction [13–15], have been also developed for sample preparation.

Besides the above-mentioned ME methods, dispersive liquid–liquid microextraction (DLLME), first developed by Rezaee et al. in 2006 [16], is considered a convenient and efficient ME technique. DLLME routinely exhibits a high extraction efficiency, improved stability, the potential for enhanced sensitivity, and a simplified sample pretreatment procedure compared to other ME methods. The method is based on a ternary component solvent system that is formed after injecting an appropriate mixture of a water-immiscible extraction solvent and a water-miscible dispersive solvent into an aqueous sample solution. The mixture quickly reaches equilibrium, which dramatically shortens the operation time. DLLME has been widely applied to the determination of pesticides [17–19], organic and inorganic environmental contaminants [20–24], and pharmaceuticals [25–27] in various matrices.

In recent years, ionic liquid (IL) have attracted increased attention as alternatives to environmentally unfriendly

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Abbreviations: **ANOVA**, analysis of variance; **ArPPE**, aryloxyphenoxy-propionate herbicide; **$[C_8MIM]Cl$**, 1-octyl-3-methylimidazolium chloride; **$[C_8MIM]NTf_2$**, 1-octyl-3-methylimidazolium bis[(trifluoromethane)sulfonyl]imide; **CCD**, central composite design; **IL**, ionic liquid; **DOE**, design of experiments; **$LiNTf_2$**, lithium bis[(trifluoromethane)sulfonyl]imide; **LPME**, liquid-phase microextraction; **RSM**, response surface methodology; **USA DLLME**, ultrasound-assisted DLLME

extractants, such as hydrocarbons and chlorinated hydrocarbons [16, 22, 28–30]. IL-based ME techniques [31–37] have achieved good results with regard to the pretreatment of environmental samples. IL-based DLLME has also received a great deal of attention recently, not only with respect to traditional DLLME methods, but also to modified and innovative DLLME methods [38–42]. One modified approach to IL-DLLME utilizes ultrasound or heat to disperse the IL phase. The use of ultrasound or a cool-down procedure assists the mass transfer process. Another innovative IL-DLLME method uses an equimolar in situ metathesis (halide exchange) reaction (in situ IL-DLLME) [42] to form a turbid solution. In this method, a small amount of hydrophilic IL is first dissolved in an aqueous solution, and the in situ halide exchange reaction is then performed after adding the ion exchange reagent (e.g. lithium bis[(trifluoromethane)sulfonyl]imide [$LiNTf_2$]). The formation of a hydrophobic IL and the extraction occurs simultaneously, which greatly simplifies the operation and reduces the extraction time.

Different IL-DLLME methods have unique advantages. In the present study, a novel method was developed that unites the ultrasound-assisted DLLME (USA DLLME) and in situ IL-DLLME methods into one extraction procedure. In this new method, a mixture of hydrophilic IL and an organic solvent was injected into the aqueous solution to perform the first extraction (USA DLLME). A hydrophilic IL was used as a dispersive solvent due to its good solubility in water. Pretreatment via ultrasonication was used to enhance the dispersion and accomplish the first extraction process. Following ultrasonication, $LiNTf_2$ was injected, and the halide exchange reaction occurred (Supporting Information Fig. S1) to form the extraction IL phase in situ. The halide exchange reaction resulted in the second extraction (in situ IL-DLLME). The dispersive solvent in the first extraction (i.e. IL) became the extraction solvent and was collected during the second extraction. Therefore, the extraction is made more efficient by completely removing any remainder of dispersive solvent that could increase the solubility of analytes in the aqueous phase. Finally, a mixture of organic solvent and IL containing the extracted compounds is obtained. A schematic diagram of the method is shown in Fig. 1. In this study, the sequential DLLME was demonstrated to be more efficient than widely used DLLME procedures for the analysis of certain studied compounds in water samples.

Aryloxyphenoxy-propionate herbicides (ArPPEs) are a class of fatty acid synthesis inhibitors. They act on acetyl-CoA carboxylase (ACCase), which catalyzes the transformation of acetyl-CoA to malonyl-CoA during the initial step of fatty acid synthesis. ArPPEs exhibit a negative effect on the synthesis of lipids, resulting in the inhibition of the production of cell membranes, cytoplasmic membranes, or other waxy substances. This type of herbicide is toxic to aquatic organisms, especially fish. Haloxyfop-R-methyl, cyhalofop-butyl, fenoxaprop-P-ethyl, and fluazifop-P-butyl are widely used ArPPEs in agricultural practices, and the accumulation of these herbicides could potentially pollute and destroy fish populations in natural water systems. Therefore, it is necessary to develop robust methods to analyze ArPPE residues in water.

To the best of our knowledge, with the exception of fluazifop-p-butyl, microextraction techniques have not been specifically applied to the extraction of ArPPE herbicides from water samples, and there have been no reports describing the above-mentioned combination of the two extraction procedures. The aim of the current work is to apply the proposed sequential DLLME method followed by HPLC to the preconcentration and determination of four ArPPE herbicides in water samples. The effect of certain variables, including the amount of IL, the volume of organic solvent, the ultrasonication time, the pH, and the salt concentration, on the extraction recovery (ER) and enrichment factor (EF) of each herbicide was evaluated using a central composite design (CCD) that was based on the response surface methodology (RSM). Using a CCD, the experimental procedure was optimized and the performance was compared with widely used DLLME methods. Finally, the present method was successfully applied to the determination of the four herbicides in real water samples (river water, reservoir water, and tap water).

2 Experimental

2.1 Reagents

The herbicide standards (haloxyfop-R-methyl, cyhalofop-butyl, fenoxaprop-P-ethyl, and fluazifop-P-butyl) were obtained from the Agricultural Environmental Protection Institution (Tianjin, China). The compounds 1-octyl-3-methylimidazolium chloride ([C_8MIM]Cl) and 1-hexyl-3-methylimidazolium chloride ([C6MIM]Cl) were obtained from the Centre for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). $LiNTf_2$ and chlorobenzene were purchased from Aladdin Chemistry (Shanghai, China). HPLC-grade methanol was purchased from Dikma Technologies (Lake Forest, CA, USA). Analytical-grade chloroform, 1,1,2,2-tetrachloroethane, sodium chloride, potassium dihydrogen phosphate, and potassium hydroxide were obtained from the Beijing Chemical Factory (Beijing, China).

Stock solutions of the herbicide standards (1 mg mL^{-1}) were prepared in HPLC-grade methanol and were stored in a refrigerator. Mixed standard solutions were also prepared in methanol. The working standard solutions were prepared daily by diluting the mixed standard solutions to different concentrations using ultrapure water. Tap water, river water, and reservoir water from Beijing, China, were collected in glass bottles for method validation. The real water samples were stored in the refrigerator, protected from light, and filtered through a 0.22-μm membrane before use.

2.2 Instrumentation and software

The chromatographic analysis was conducted on an Agilent 1200 HPLC system that was equipped with a variable

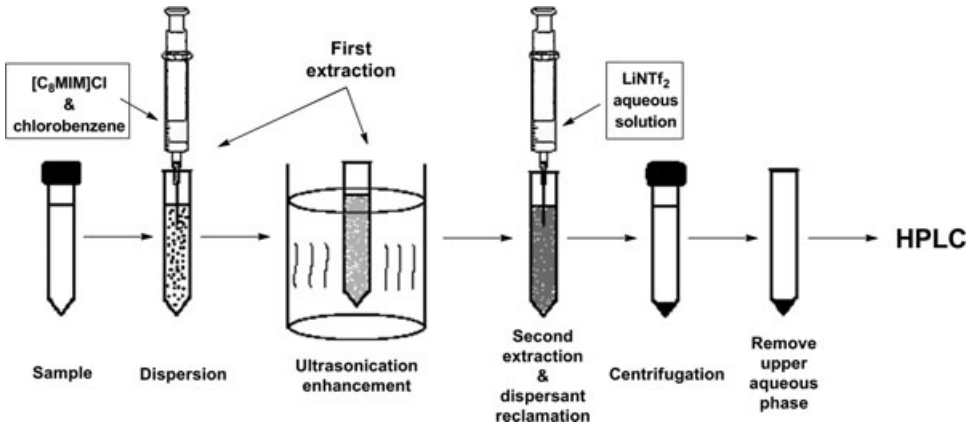

Figure 1. The schematic diagram of the sequential DLLME method.

wavelength detector (VWD) (Santa Clara, CA, USA). A high-pressure injection valve fitted with a 20-μL loop was used for sample injection. Separation of the analytes was performed on an Agilent Eclipse Plus C18 column (5 μm, 4.6 mm × 250 mm). The KQ-50DE ultrasonic water bath that was used for ultrasonication of the samples was purchased from Kunshan Ultrasonic Instruments Co., Ltd. (Kunshan, China). Centrifugation was performed in a BAIYANG 52A centrifuge from the Baiyang Centrifuge Factory (Xin'an, China).

Optimization of the various parameters that affected the extraction in the sequential DLLME was performed by a half-fraction CCD using MINITAB® Release 16 Statistical Software (State College, PA, USA) [43].

2.3 Chromatographic conditions

The flow rate of the mobile phase was maintained at 1 mL min^{-1}. Mobile phases A and B were water and methanol, respectively. The gradient conditions were as follows: 0–1 min, 70% B; 1–20 min, 70–80% B; 20–25 min, 80% B; 25–30 min, 80–70% B; and 30–35 min, 70% B. Absorbance was measured at a wavelength of 238 nm.

2.4 Extraction procedure

2.4.1 Sequential DLLME procedures

A total of 8 mL of each of the standard solutions or water samples was placed into a 10-mL glass centrifuge tube, and pH and NaCl concentration of the solutions were pre-adjusted to 6.4 and 4.6 (%, m/v), respectively. A mixture of 10 mg $[C_8MIM]Cl$ and 30 μL chlorobenzene was subsequently injected into the sample solution. The resulting dispersion was then ultrasonicated at a frequency of 40 kHz and a power of 50 W for 2.0 min. During the ultrasonication process, the solution became cloudy due to the dispersion of fine chlorobenzene droplets in the sample. After ultrasonication, an aqueous solution of $LiNTf_2$ (415 μL, 0.03 g mL^{-1}) was added to each tube, and the cloudy solution became more turbid with the formation of immiscible $[C_8MIM]NTf_2$. After gently shaking, the turbid mixture was centrifuged at 4000 rpm for 10 min. The mixture of chlorobenzene and $[C_8MIM]NTf_2$ containing the extracted compounds settled at the bottom of the tube, and the upper aqueous phase was removed with a syringe. Approximately 38 μL of the sedimented phase was obtained and an aliquot of 10 μL from the final solution was directly injected into the HPLC system for analysis.

2.4.2 In situ IL-DLLME procedures

A total of 0.03 g of $[C_8MIM]Cl$ was added to a glass centrifuge tube. Then, 8 mL of a spiked water sample whose pH and NaCl concentration were pre-adjusted were placed into the tube. After shaking, the IL completely dissolved into the water sample. An aqueous solution of $LiNTf_2$ (1250 μL, 0.03 g mL^{-1}) was added to the tube, and a cloudy solution was formed. After gently shaking, the turbid mixture was centrifuged at 4000 rpm for 10 min. The upper aqueous phase was removed with a syringe, and approximately 39 μL of sedimented phase was obtained. Aliquot of 10 μL from the final solution was directly injected into the HPLC system for analysis.

2.4.3 Conventional and USA DLLME procedures

A total of 8 mL of the spiked water sample whose pH and NaCl concentration were pre-adjusted was placed into a glass centrifuge tube. A mixture containing 45 μL chlorobenzene and 900 μL methanol was quickly injected into the sample. For the USA DLLME, the resulting solution was ultrasonicated for 2.0 min to enhance the dispersion and extraction. Then, the turbid mixture was centrifuged at 4000 rpm for 10 min. The upper aqueous phase was removed with a syringe, 35 μL (in DLLME) and 31 μL (in USA DLLME) of the sedimented phase were obtained in the conventional DLLME and USA DLLME methods, respectively, and aliquots of 10 μL from each solution were directly injected into the HPLC system for analysis.

3 Results and Discussion

3.1 Selection of the extraction solvents

The first step during the development of a DLLME procedure is to select the appropriate extractant and dispersant mixture. In this study, the selection included an appropriate organic solvent and the IL. Because various chlorinated hydrocarbons, such as chlorobenzene, chloroform, and 1,1,2,2-tetrachloroethane, have been successfully used as extraction solvents [21, 26, 37], these compounds were selected for optimization. Additionally, $[C_6MIM]Cl$ and $[C_8MIM]Cl$ were selected and compared for the same reason.

During the first extraction process, 1,1,2,2-tetrachloroethane did not exhibit good dispersion in the aqueous solution, even after ultrasonication. Dispersion did not improve until the much more dispersive IL solvent was added. Chloroform and chlorobenzene were able to disperse in the solution using less of the dispersing solvent. However, chloroform volatilized extensively during the ultrasonication process due to its high vapor pressure (21.28 kPa/20°C). The high volatility of the chloroform resulted in a decrease of the volume of extract after centrifugation, which led to an unacceptably low recovery. Therefore, chlorobenzene (vapor pressure 1.33 kPa/20°C) was chosen as the best organic extraction solvent for the first extraction step. In the case of IL, the organic solvent exhibited improved dispersion in the solution when $[C_8MIM]Cl$ was used compared with $[C_6MIM]Cl$. Furthermore, the solubility of $[C_8MIM]NTf_2$ is lower than that of $[C_6MIM]NTf_2$, making the former more efficient during the second extraction. Thus, chlorobenzene and $[C_8MIM]Cl$ were used as extraction solvents for the sequential DLLME method.

3.2 Optimization of the procedure using an RSM approach

Following some preliminary experiments, the optimization of the extraction conditions was conducted using a half-fraction CCD. The range of variables affecting the ER and EF is represented in Supporting Information Table S1; these variables include the amount of IL, the volume of organic solvent, the ultrasonication time, the pH, and the concentration of salt. The EF and ER (%) for each herbicide were taken as the responses, meaning those eight responses were simultaneously analyzed. It is impractical to discuss the regressions of all eight responses, so ER1 and EF1 were selected to represent all cases. All other results are shown in the tables.

The design matrix, which includes the responses (experimental values), is given in Supporting Information Table S2. All experiments were performed using working solutions that contained 50 $\mu g\ L^{-1}$ of each herbicide.

Multiple regression results obtained from CCD, including *t*- and *p*-values along with the constants and coefficients (estimated in coded units), are given in Supporting Information Table S3. The *t*-value was used to determine the significance of the regression coefficients for the experimental parameters, and the *p*-value was defined as the smallest level of significance that would lead to the rejection of the null hypothesis [44]. The coefficient terms that had a large value of t and a small value of p were considered more significant than the others. For example, the effect of the linear terms, including the amount of IL, the volume of organic solvent, the pH and the concentration of salt, were found to be significant with respect to the ER1 and EF1 results because the *p*-values were less than 0.05. The quadratic terms of the responses were not significant except for the volumes of IL ($p = 0.031$), chlorobenzene ($p = 0.001$), pH ($p = 0.014$) in the regression of EF1, and pH ($p = 0.008$) in the regression of ER1, indicating that the variables exhibit a quadratic response with ER1 and EF1. The R^2 and adjusted R^2 statistics and SDs for the residuals in the regression model are listed in Supporting Information Table S4. The R^2 statistics indicated that the models displayed variability in the range of 93.57–99.43%. The adjusted R^2 statistics ranged from 75.20 to 97.79%, which indicated a high dependence and coefficient of estimation between the experimental and the predicted response values. The SDs of the residuals were $\leq$7.4 for all variables except EF4 (10.016). This finding confirmed that the regression adequately described the relationships between the experimental responses and the variables.

The results of the analysis of variance (ANOVA) are presented in Supporting Information Table S5. In the ANOVA study, a *p*-value lower than 0.05 indicated the statistical significance of an effect with 95% confidence interval, implying that the model is statistically significant [45]. The integrated regressions for ER1 and EF1 were significant because the *p*-values were 0.016 and 0.000, respectively. The linear ($p = 0.004$) and square terms ($p = 0.039$) for ER1 were significant, but the coefficient of interaction ($p = 0.091$) was not. All three effects were significant in the regression for EF1. The Lack of Fit (LOF) *p*-values were 0.504 for ER1 and 0.415 for EF1, which are much higher than 0.05. The large *p*-values indicated that the LOF was not significant relative to the pure error. Thus, the applicability of the predicted model was confirmed through this ANOVA study. The normality of each data point was checked using a normal probability plot (NPP) of the residuals.

Three-dimensional (3-D) response surfaces were constructed to visualize the relationship between the responses and the significant experimental factors [46, 47]. These surfaces led to a better understanding of the individual and cumulative effects of the variables and of the mutual interactions between the independent and dependent variables. The response surfaces of ER1 and EF1 versus the significant parameters, including IL volume, chlorobenzene volume, pH, and NaCl concentration, are shown in Supporting Information Figs. S2 and S3, respectively.

The final optimization of the experimental conditions was performed using optimization plots, which helped to identify the variable settings that were required to obtain a desired response. In the present study, with the goal of

Table 1. Analytical parameters for the determination of aryloxyphenoxy-propionate herbicides in water samples by the sequential DLLME–HPLC method

Herbicide	Linear range ($\mu g\ L^{-1}$)	Linearity	r	LODs ($\mu g\ L^{-1}$)[a)]	RSD (%)[b)]	Enrichment factor[c)]	Recovery (%)[c)]
Haloxyfop-R-methyl	15–300	$y = 2.49x - 7.29$	0.9997	4.35	3.12	171	78.4
Cyhalofop-butyl	10–300	$y = 4.68x - 0.18$	0.9997	1.60	2.92	192	91.0
Fenoxaprop-P-ethyl	10–300	$y = 7.08x - 33.06$	0.9994	1.50	4.23	173	82.2
Fluazifop-P-butyl	20–300	$y = 1.82x - 3.00$	0.9994	6.12	5.44	179	85.2

a) LODs are calculated from the water samples spiked with 20 $\mu g\ L^{-1}$ of each herbicide, S/N = 3.
b) RSD values are calculated by five extraction reduplicates ($n = 5$) of the studied herbicides.
c) The extraction recovery and enrichment factor are obtained at the spiked level of 50 $\mu g\ L^{-1}$.

finding the maximum for each response (i.e. from ER1 and EF1 to ER4 and EF4) at reasonable operating conditions, the experimental factors were optimized at the following conditions: 9.44 mg [C_8MIM]Cl, 29.60 μL chlorobenzene, ultrasonication for 2.0 min, pH of 6.37, and 4.59% NaCl concentration, with a desirability score of 0.9553. For convenience of operation, 10 mg IL, 30 μL chlorobenzene, a pH of 6.4, and an NaCl concentration of 4.6 (%, m/v) were used.

3.3 Comparison between sequential DLLME and widely used DLLME methods

To confirm the improved results that were obtained by sequential DLLME with respect to commonly used DLLME methods, the proposed method was compared with the conventional DLLME, USA DLLME, and in situ DLLME procedures. For the purpose of obtaining near equal volumes of sedimented extract, 30 mg [C_8MIM]Cl and 45 μL chlorobenzene were used throughout the different DLLME methods. The operation of each method is described in Section 2.4. To quantitatively assess the performance of each technique, EFs were determined and are listed in Supporting Information Table S6. Compared with the in situ IL-DLLME, the higher EFs of the sequential DLLME indicated that chlorobenzene was more suitable than ILs for the extraction of ArPPEs. Additionally, the sequential DLLME showed better performance than the chlorobenzene-based conventional DLLME and the USA DLLME except for the extraction of haloxyfop-R-methyl with USA DLLME. These results could be attributed to the fact that the methanol (0.9 mL) that was added into the water increased the solubility of the other three herbicides and increased the extraction difficulty for chlorobenzene. In sequential DLLME, the very small amount of [C_8MIM]Cl has little effect on the herbicide solubility, but it reduces the size of the chlorobenzene droplets. Although the extraction mixture did not disperse very well in the solution, the size of the chlorobenzene droplets decreased with the aid of the miscible [C_8MIM]Cl compared with solutions containing no IL. This reduction in droplet size helped the ultrasonication disperse the chlorobenzene more easily. In addition, after the second extraction, no reagent remained in the aqueous solution. Thus, the proposed method improved the extraction efficiency compared with the commonly used DLLME procedures.

3.4 Evaluation of method performance

The sequential DLLME method was evaluated according to linearity, LODs, precision, EFs, and recoveries under the above-optimized conditions. The validated results are shown in Table 1. Linearity was observed from 10 to 300, 15 to 300, and 20 to 300 $\mu g\ L^{-1}$, with correlation coefficients (r) ranging from 0.9994 to 0.9997. The precision was obtained by testing five replicates of water samples that were spiked with 50 $\mu g\ L^{-1}$ of herbicide. The RSDs of the herbicides ranged from 2.9 to 5.4%. The LODs, which were determined as the analyte concentration that yielded a S/N ratio of 3 as calculated by the instrument software at a spiked level of 20 $\mu g\ L^{-1}$ and then experimentally tested, ranged from 1.50 to 6.12 $\mu g\ L^{-1}$. The EFs ranged from 171 to 192, which were

Table 2. Comparison of the sequential DLLME–HPLC-UV method with other methods for the determination of ArPPEs in aqueous samples

Method	Sample volume (mL)	Extraction time (min)	LODs ($\mu g\ L^{-1}$)	LR ($\mu g\ L^{-1}$)	References
SPE-HPLC-ISI-MS	2000	>30	0.003–0.01	0.01–0.5	[48]
Buffered QuEChERS-UPLC-MS/MS	10	4	3.0	5–100	[49]
HF LPME-UPLC-MS/MS[a)]	15	45	0.09	5–100	[50]
The presented method	8	3	6.1	10–300	—

a)Hollow fiber liquid-phase microextraction.

Table 3. Relative recoveries and the relative SDs in three spiked water samples by the sequential DLLME–HPLC method

Herbicide	Spiked level (μg L^{-1})	Reservoir water		River water		Tap water	
		RR[a] (%)	RSD[b] (%)	RR (%)	RSD (%)	RR (%)	RSD (%)
	Blank	N.D.[c]		N.D.		N.D.	
Haloxyfop-R-methyl	25	99.7	5.2	108.3	4.6	114.8	4.9
	50	107.6	2.3	96.4	5.6	103.7	5.9
	Blank	N.D.		N.D.		N.D.	
Cyhalofop-butyl	25	108.0	1.1	108.8	3.8	112.8	4.9
	50	108.3	2.7	102.6	8.5	110.6	7.8
	Blank	N.D.		N.D.		N.D.	
Fenoxaprop-P-ethyl	25	96.8	2.1	101.0	5.2	111.2	1.5
	50	101.1	3.1	94.6	5.3	101.5	9.1
	Blank	N.D.		N.D.		N.D.	
Fluazifop-P-butyl	25	95.89	8.72	77.03	9.7	89.8	8.27
	50	89.76	5.55	96.58	7.98	87.04	4.34

a) RR, relative recovery.
b) RSD values were calculated by performing three extraction replicates ($n = 3$) of the studied herbicides.
c) N.D., not detected

in good agreement with the predicted values. The extraction and the determination of ArPPEs using the proposed method were compared with other methods [48–50], and the results are shown in Table 2. Table 2 shows that sequential DLLME uses a shorter extraction time than the other methods and consumes less sample. Furthermore, the method of easiest operation could achieve performances close to other methods without employing advanced instruments. Therefore, in the future, sequential DLLME is expected to be widely applied to the analysis of target compounds in aqueous samples.

3.5 Real water sample analysis

The applicability of the sequential DLLME method was validated by performing extractions in three real water samples, including reservoir water, river water, and tap water, at spiked levels of 25 and 50 μg L^{-1}. The recoveries and RSDs are shown in Table 3. The results indicated that the recoveries were between 77.0 and 114.8% for the three water samples. The RSDs were between 1.1 and 9.7%. These results indicated that the matrices of the real water samples had little effect on the proposed sequential DLLME method for the preconcentration of ArPPEs from water samples. The typical chromatograms of the nonspiked and spiked river water samples obtained by the sequential DLLME method are shown in Fig. 2.

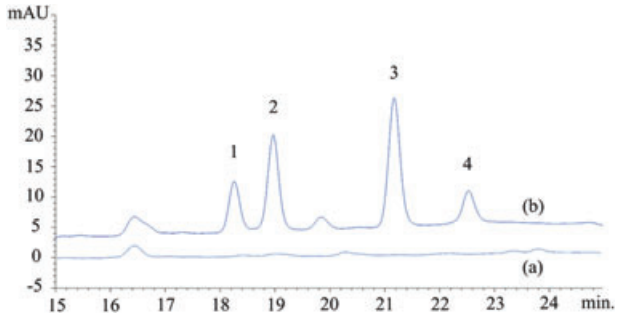

Figure 2. Chromatograms of aryloxyphenoxy-propionate herbicides in a (a) blank and (b) spiked (at the concentration level of 50 μg L^{-1}) river water sample obtained by sequential DLLME. Peaks: (1) haloxyfop-R-methyl, (2) cyhalofop-butyl, (3) fenoxaprop-P-ethyl, and (4) fluazifop-P-butyl.

4 Concluding remarks

In this study, a novel sequential DLLME was developed that combined USA DLLME and in situ IL-DLLME into one extraction procedure. The IL dispersive solvent during the first extraction became the extraction solvent and was collected during the second extraction. Parameters affecting the experimental results were analyzed and optimized with the help of design of experiment (DOE). The extraction method, followed by HPLC-UV analysis, was applied and shown to be superior over the common DLLME methods for the determination of ArPPEs in water samples. The fast, simple, and sensitive sequential DLLME method is expected to be widely applied to the screening of target compounds for extractions from aqueous samples in the future.

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