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Research Article

Comparison of two ultrasound-enhanced microextractions combined with HPLC for determining acaricides in water

An ultrasound-enhanced *in situ* solvent formation microextraction has been developed first time and compared with ultrasound-enhanced ionic-liquid-assisted dispersive liquid–liquid microextraction for the HPLC analysis of acaricides in environmental water samples. A ionic liquid ($[C_8MIM][PF_6]$) was used as the green extraction solvent through two pathways. The experimental parameters, such as the type and volume of both of the extraction solvent disperser solvent, ultrasonication time, and salt addition, were investigated and optimized. The analytical performance using the optimized conditions proved the feasibility of the developed methods for the quantitation of trace levels of acaricides by obtaining limits of detection that range from 0.54 to 3.68 μg/L. The *in situ* solvent formation microextraction method possesses more positive characteristics than the ionic-liquid-assisted dispersive liquid–liquid microextraction method (except for spirodiclofen determination) when comparing the validation parameters. Both methods were successfully applied to determining acaricides in real water samples.

Keywords: Acaricides / High-performance liquid chromatography / Ionic liquid / Water
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1 Introduction

Acaricides are used primarily for controlling mites on farmland and in orchards. Acaricides such as chlorfenapyr and diafenthiuron are excellent broad-spectrum insecticide-acaricides and they are widely applied in the control of pests on crops [1–3]. However, residues of acaricides can be transferred from farming soil to the environment and can be found in river water. Several studies have examined both chlorfenapyr and diafenthiuron, including Shan's work and the US Environmental Protection Agency's toxicity studies on aquatic organisms, indicating that these two acaricides are potential hazards to aquatic organisms [4–6]. Therefore, it is necessary to monitor the water quality because contamination not only affects human health but it also disrupts the normal endocrine function of aquatic life [7]. In this regard, sensitive, precise, and accessible analytical methods are indispensable for measuring acaricides in environmental samples.

Microextraction techniques have become popular over the last few years as suitable multiresidual analytical methods due to their favorable characteristics, such as reduced cost and the complete elimination of toxic organic solvents [8]. Dispersive liquid–liquid microextraction (DLLME) was developed in 2006 to enhance the contact surface area between the sample and the extractant phase by the efficient dispersion of the extractant into the aqueous solution [9]. In DLLME, a disperser solvent is used as a third phase to form minute drops of extractant along the aqueous samples, which make the sample and extractant phase miscible. Ionic liquids (ILs) have been proposed as extractants instead of organic solvent in DLLME as potential green solvent. ILs are organic salts formed by organic cations and either organic or inorganic anions. These compounds have unique physical properties, such as low vapor pressure, favorable thermal stability, good extractive capability for various compounds, and water miscibility. Additionally, ILs can be designed to be miscible or immiscible due to the tunable solvation properties [10, 11]. With the help of a disperser, drops of ILs can be dispersed entirely into aqueous solution. However, the use of a disperser may decrease the extractability of hydrophobic analytes and thus

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Abbreviations: EF, enrichment factor; **IL**, ionic liquid; **IL-DLLME**, ionic liquid-assisted dispersive liquid–liquid microextraction; **ISFME**, *in situ* solvent formation microextraction

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reduce the extraction recovery [12]. *In situ* solvent formation microextraction (ISFME), derived from DLLME based on the use of ILs, was proposed for the first time in 2009 by Badgadi and Shemirani [13]. The main merit of ISFME is not only its compatibility with a high salt content (40%, w/v) but also no disperser solvent is used. Under high salt conditions, phase separation can occur while it is established that the solubility of ILs increases as the concentration of salt in the solution increases [14]. The extraction process starts with a water-miscible IL dissolving completely in the sample solution, an ion-exchange reagent is added to form a water-immiscible material with the IL. It is noteworthy that in ISFME, the extraction phase (immiscible IL) is formed *in situ* while extracting analytes simultaneously, and there is no initial interface between the extractant and water phases, thus the equilibrium time is short. DLLME and ISFME based on ILs have been proposed to increase the contact surface significantly between the extractant phase and the sample.

On the other hand, ultrasonication is a powerful tool to increasing the mass transfer between two immiscible phases. This technique considerably accelerates the extraction process and increases the extraction efficiency. For this reason, ultrasound techniques have been combined with IL-DLLME to create a new method called ultrasound-assisted ionic liquid dispersive liquid–liquid microextraction (UA-IL-DLLME), which has been successfully used for the extraction and determination of different pollutants, including biogenic amines and pesticides [15, 16]. To the best of our knowledge, there has been no previous report concerning the application of ultrasound-assisted *in situ* formation microextraction (UA-ISFME). Additionally, no related work exists on the comparison of the UA-IL-DLLME and UA-ISFME methods.

In this article, UA-IL-DLLME and UA-ISFME methods are presented for extracting and determining acaricides (Fig. 1) in water samples. The *in situ* reaction used is:

$$[C_8MIM][Cl] + KPF_6 \rightarrow [C_8MIM][PF_6] + KCl$$

This paper describes interesting approaches to use the same IL ($[C_8MIM][PF_6]$) for extraction by different pathways. The extraction parameters were optimized, and the proposed methods for measuring acaricides in water samples were applied.

2 Materials and methods

2.1 Reagents and standards

Clofentezine, fenpyroximate, and pyridaben were purchased from Aladdin (Shanghai, China). Chlorfenapyr and diafenthiuron were obtained from the Agricultural Environmental Protection Institution (Tianjin, China). Spirodiclofen was obtained from Numen International Biotech (Beijing, China). Stock standard solutions were prepared in HPLC-grade acetonitrile (Dikma, China) at 50 mg/L. The working standard solutions were prepared by diluting the stock standard solutions to various concentrations in acetonitrile. 1-Hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$), 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8MIM][PF_6]$), 1-hexyl-3-methylimidazolium chloride ($[C_6MIM][Cl]$), and 1-octyl-3-methylimidazolium chloride ($[C_8MIM][Cl]$) were purchased from the Center for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). Potassium hexafluorophosphate (KPF_6) was purchased from the Aladdin. Deionized water was purified using a Milli-Q SP Reagent Water System (Millipore, Bedford, MA, USA).

2.2 Apparatus

HPLC analysis was performed using an Agilent 1200 HPLC system (CA, USA) equipped with a variable-wavelength detector and automatic sample injector. The separation was performed on a Spuril C18 column (5 μm, 4.6 × 250 mm, Dikma) using Spursil C18 Guard Cartridges (5 μm, 2.1 × 10 mm, Dikma) and an acetonitrile/water solution (74:26, v/v) as the mobile phase with a flow rate of 1 mL/min. The detection wavelengths were set to 270 nm for Clofentezine, 260 nm for chlorfenapyr, fenpyroximate, and diafenthiuron, 240 nm for pyridaben, and 230 nm for spirodiclofen. A Mettler-Toledo AL104 electronic balance (Shanghai, China), Baiyang 52A (Baoding, China) centrifuge, ultrasonic cleaner (KQ-50DE, Kunshan, China), and BF-2000 nitrogen concentrator (Beijing, China) were used in this work.

2.3 Extraction procedures

UA-IL-DLLME: 10 mL of a sample solution was placed in a 15 mL screw-cap conical-bottom tube. A mixture of 250 μL of methanol, as a dispersive solvent, and 60 μL of $[C_8MIM][PF_6]$ (extraction solvent) was rapidly injected into the water sample. A cloudy solution containing fine IL droplets formed after ultrasonic treatment for 2 min and was then centrifuged at 4000 rpm for 5 min. The supernatant was removed using a syringe, and the sedimented phase was evaporated under nitrogen. The IL phase (approximately 40 μL) was dissolved in 50 μL of acetonitrile, and 10 μL of the resulting mixture was injected into an HPLC for analysis.

UA-ISFME: 10 mL of a sample solution containing $[C_8MIM][Cl]$ (40 mg) was placed in a 15-mL screw-cap conical-bottom tube. After shaking, an excess of KPF_6 (43–45 mg) was added to this solution, and a cloudy solution formed immediately. The conical tube was subjected to ultrasonic treatment for 2 min to fully extract the analytes from the solution. The mixture was centrifuged for 5 min at 4000 rpm. The supernatant was removed with a syringe, and the sedimented phase was evaporated under nitrogen. Afterwards, the IL phase (approximately 30 μL) was dissolved in 50 μL of acetonitrile, and 10 μL of the resulting mixture was injected into an HPLC for analysis.

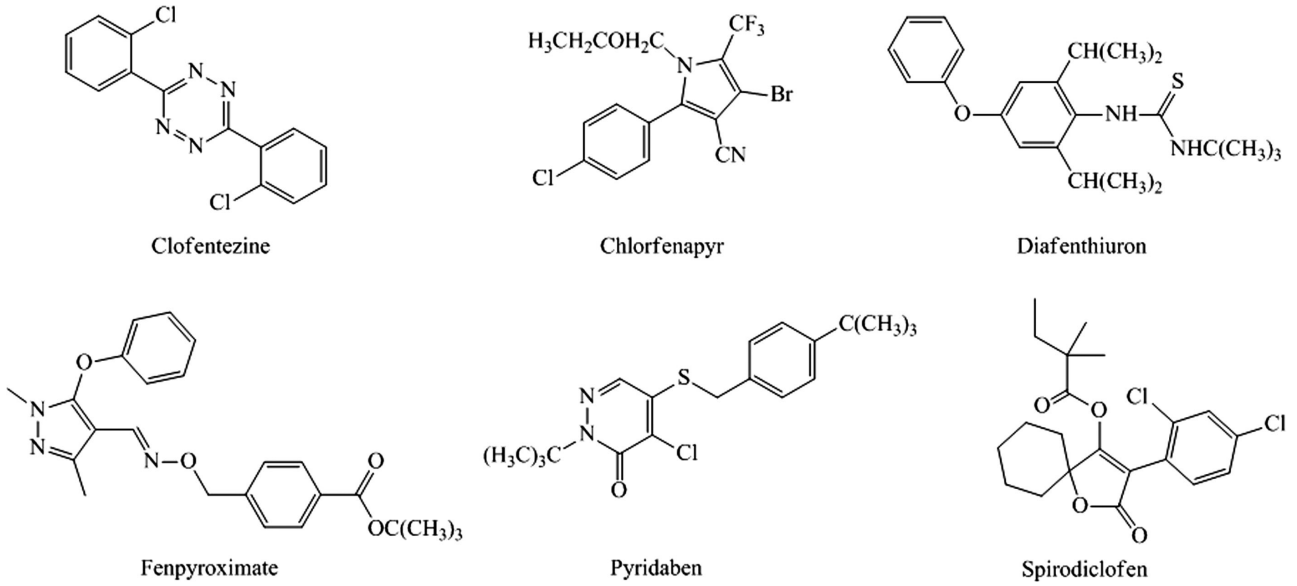

Figure 1. Chemical structures of the acaricides.

2.4 Samples

Three water samples were collected from the Nanming River (Guizhou, China) on the same day going from upstream to downstream. Each sample was stored at 4°C, centrifuged at 4000 rpm for 5 min, and filtered through a 0.22 μm membrane (Agla, USA) before use.

3 Results and discussion

In this study, the UA-IL-DLLME and UA-ISFME methods were compared in combination with HPLC. A step-by-step optimization scheme was used and included the type and volume of the extraction solvent, the type and volume of the disperser solvent, the ultrasonication time, and the addition of salt. To evaluate the performance of these proposed methods, the enrichment factors (EFs) and recoveries were calculated using Eqs. (1) and (2):

$$\mathrm{EF} = \frac{C_{\mathrm{IL}}}{C_0} \tag{1}$$

$$R = \frac{C_{\mathrm{IL}} \times V_{\mathrm{IL}}}{C_0 \times V_0} \times 100\% = \mathrm{EF} \times \frac{V_{\mathrm{IL}}}{V_0} \times 100\% \tag{2}$$

where EF, R, C_{IL}, C_0, V_{IL}, and V_0 are the enrichment factor, recovery, analyte concentration in the extraction solvent, analyte concentration in the water sample, extraction solvent volume (sedimented phase), and water sample volume, respectively.

3.1 Effect of type and dose of IL

For the DLLME procedure, an appropriate IL for extraction should possess certain features, such as low water miscibility, a higher density than water, a nonvolatile nature, and high extraction efficiency for the target analytes [11]. According to the literature, 1-alkyl-3-methylimidazolium hexafluorophosphate ($[C_n\mathrm{MIM}][PF_6]$, $n = 6$ and 8) is appropriate and has been used widely for DLLME analyses [16, 17]. Therefore, the extraction efficiency of $[C_6\mathrm{MIM}][PF_6]$ and $[C_8\mathrm{MIM}][PF_6]$ was studied. $[C_8\mathrm{MIM}][PF_6]$ exhibited better dispersive behavior and extraction results than $[C_6\mathrm{MIM}][PF_6]$ at the same dosage (50 μL). The recoveries ranged from 65.58–88.09% when using $[C_8\mathrm{MIM}][PF_6]$ as the extraction solvent while the recoveries were below 6.68% when using $[C_6\mathrm{MIM}][PF_6]$. However, the UA-ISFME procedure requires the reaction between the water-miscible IL and ion-pairing agent to form a poorly soluble, water-immiscible IL [13]. To compare the extraction efficiency of ILs containing $[PF_6]$ anions, 1-alkyl-3-methylimidazolium chloride ($[C_n\mathrm{MIM}][\mathrm{Cl}]$, $n = 6$ and 8) was chose to react with KPF_6. As a result, $[C_6\mathrm{MIM}][\mathrm{Cl}]$ demonstrated a lower extraction efficiency (below 0.85%) than $[C_8\mathrm{MIM}][\mathrm{Cl}]$ for the UA-ISFME procedure at the same dosage (30 mg). Therefore, $[C_8\mathrm{MIM}][PF_6]$ and $[C_8\mathrm{MIM}][\mathrm{Cl}]$ were selected for the subsequent UA-IL-DLLME and UA-ISFME experiments, respectively.

The volume proportion of the extraction solvent is a crucial parameter that affects the mass transfer of analytes from the water sample to the extraction phase. To study the effect of the IL dose on the extraction efficiency, additional experiments were performed using 250 μL methanol containing different doses (i.e., 40, 45, 50, 55, 60, and 70 μL) of $[C_8\mathrm{MIM}][PF_6]$ and $[C_8\mathrm{MIM}][\mathrm{Cl}]$ over the range of 20–50 mg. As shown in Supporting Information Fig. S1, the extraction efficiency increases slightly with increasing $[C_8\mathrm{MIM}][PF_6]$ volume up to 60 μL due to the increase in the IL phase volume. Further increasing the $[C_8\mathrm{MIM}][PF_6]$ volume resulted in a slight decrease in the R of acaricides. When the $[C_8\mathrm{MIM}][PF_6]$ volume reached a specific level, the extraction performance

would reach an equilibrium. If the $[C_8MIM][PF_6]$ volume exceeded this level, the final IL phase obtained after separation from solution would be excessive to result in a decrease of the concentration of the analytes in it. Instead of increasing the extraction efficiency, the increase of the IL dose declined the EF of acaricides. As a result, the sensitivity for the determination of acaricides declined as well. Thus, the best choice for $[C_8MIM][PF_6]$ is 60 μL, which resulted in the highest extraction efficiency for UA-IL-DLLME. Supporting Information Fig. S1 shows that the effect of $[C_8MIM][Cl]$ on the acaricide extraction contradicts two aspects of the $[C_8MIM][PF_6]$ extraction. The highest extraction efficiencies were obtained when 40 mg $[C_8MIM][Cl]$ was used, except for spirodiclofen. Therefore, 40 mg $[C_8MIM][Cl]$ was chosen for UA-ISFME.

3.2 Effect of disperser solvent type and volume

In the UA-IL-DLLME procedure, fine IL droplets form and disperse when the IL is rapidly injected into the water sample along with the disperser solvent. Meanwhile, an appropriate disperser should be miscible in both the IL and aqueous phase. Therefore, several disperser solvents were studied, including acetonitrile, acetone, and methanol. A cloudy solution was then formed directly upon injection of the extraction solvent into the water sample with all of these disperser solvents. Methanol helped the IL obtain the best extraction efficiency, especially for diafenthiuron. These results are shown in Supporting Information Fig. S2. Therefore, methanol was used for all further studies.

The sedimented phase volume and extraction efficiency are affected by the disperser solvent volume. Experiments were performed using different methanol volumes (200, 250, 300, 350, 400, and 450 μL) to optimize the effect of the disperser volume on the extraction performance. The results (Supporting Information Fig. S3) showed that the extraction efficiency first increased and then gradually decreased upon increasing the methanol from 200 to 450 μL. Therefore, 250 μL of methanol was selected for UA-IL-DLLME during this work.

3.3 Effect of ultrasonication time

Dispersion is the key step in the extraction procedure. Ultrasound can accelerate and enhance the formation of a cloudy solution of the extraction solvent and water sample. Hence, the ultrasonication time plays an important role in both the UA-IL-DLLME and UA-ISFME procedures. A series of time intervals were investigated over the range of 0–4 min with the ultrasonic power fixed at 50 W. A similar trend existed in both procedures as observed in Supporting Information Fig. S4, extending the ultrasonication to 2 min had a positive effect on the formation of a completely cloudy solution and increased the acaricide extraction efficiency. Ultrasonication accelerated the dissolution and diffusion of KPF_6 since it was solid at first. However, the extraction efficiency decreased from 2 to 4 min after the extraction equilibrium was achieved. After 2–4 min of ultrasonic treatment, heat was generated and the temperature of solution increased. As a result, the solubility of IL in the solution was increased and the extraction efficiency was decreased accordingly. A similar phenomenon was reported in Chen's work [18]. Consequently, 2 min of ultrasonication was chosen for the UA-IL-DLLME and UA-ISFME.

3.4 Effect of salt addition

Ionic strength is considered important for improving the extraction efficiency and has been examined by adding NaCl to the sample solution. In this work, varying amounts of NaCl ranging from 0–9% (w/v) were investigated. The results showed that the extraction efficiencies decreased upon the addition of NaCl for both the UA-IL-DLLME and UA-ISFME procedures. In UA-IL-DLLME, the possible reason for these results could be the enhancement of the ion-exchange process that will in turn affect the $[C_8MIM][PF_6]$ solubility in the aqueous phase with the added salt. In UA-ISFME, these results were caused when another salt (KCl) was added from the *in situ* reaction, to form a dual-salt system resulting in the decrease of the extraction efficiencies. To best of our knowledge, no reference about a dual-salt system in microextraction was reported. In order to provide the details of this contribution, more experiments should be carried out to study in detail the effect of the dual salt. Hence, NaCl was not added in subsequent experiments.

Based on the previous discussion, the optimal conditions for the UA-IL-DLLME procedure were as follows: 10 mL of the water sample, 60 μL of $[C_8MIM][PF_6]$ (extraction solvent), 250 μL of methanol (disperser solvent), 2 min of ultrasonication, and no salt addition. For the UA-ISFME procedure: 10 mL of the water sample, 40 mg of $[C_8MIM][Cl]$, 43–45 mg of KPF_6 (ion-pairing agent), 2 min of ultrasonication, and no salt addition.

3.5 Analytical characteristics of the methods

To evaluate the proposed methods (i.e., UA-IL-DLLME and UA-ISFME), further experiments on the linearity, repeatability, LOD, and EF were performed using the optimized working conditions in distilled water. The results are shown in Table 1. Satisfactory correlation coefficients (r^2) ranging from 0.9992–0.9998 were obtained for the concentration range from 10–200 μg/L for chlorfenapyr and 5–200 μg/L for the other five analytes using UA-IL-DLLME, while the UA-ISFME method obtained 0.9994–0.9999 for six acaricides over the range from 5–200 μg/L. Calibration curves were created by plotting the peak area versus the concentration. The repeatability, described by the RSD, was investigated using five replicated analyses of standards with a concentration of 50 μg/L for each acaricide. As observed in Table 1, the obtained RSD values ranged from 0.2% (spirodiclofen) to 4.2% (diafenthiuron) for UA-IL-DLLME and 1.7%

Table 1. Parameters of the UA-IL-DLLME and UA-ISFME

Compounds	Linear equations	Linear range (μg/L)	r^2[a]	LOD[b] (μg/L)	RSD[c] (%)	EF[d]
UA-IL-DLLME:						
Clofentezine	$y = 9569.1x + 4.1769$	5–200	0.9998	2.15	2.4	247.0
Chlorfenapyr	$y = 3656.5x - 19.42$	10–200	0.9996	3.68	3.8	245.0
Fenpyroximate	$y = 6028x + 7.2504$	5–200	0.9995	1.12	1.1	242.0
Diafenthiuron	$y = 5180.9x + 1.9918$	5–200	0.9996	1.08	4.2	208.3
Pyridaben	$y = 6071.2x - 9.7877$	5–200	0.9992	1.12	2.0	209.9
Spirodiclofen	$y = 5290.5x - 20.279$	5–200	0.9992	0.85	0.2	210.9
UA-ISFME:						
Clofentezine	$y = 12539x - 15.224$	5–200	0.9999	1.48	1.7	278.3
Chlorfenapyr	$y = 4376.8x + 0.7237$	5–200	0.9997	1.71	2.9	256.7
Fenpyroximate	$y = 6912.2x - 17.008$	5–200	0.9997	0.92	3.8	248.4
Diafenthiuron	$y = 6383.6x + 3.9859$	5–200	0.9996	0.62	2.2	248.8
Pyridaben	$y = 6682.5x - 18.762$	5–200	0.9997	0.54	3.3	225.6
Spirodiclofen	$y = 2640x - 17.82$	5–200	0.9994	1.16	2.6	100.9

a) r^2: correlation coefficient.
b) LOD for S/N = 3.
c) RSD at concentration of 50 μg/L ($n = 5$).
d) EF at concentration of 50 μg/L.

(Clofentezine) to 3.8% (fenpyroximate) for UA-ISFME. The LOD for the acaricides, calculated as a S/N of 3, ranged from 0.85–3.68 μg/L for the UA-IL-DLLME method and from 0.54–1.71 μg/L for the UA-ISFME method. The EFs were between 208.3 and 247.0 for UA-IL-DLLME and between 100.9 and 278.3 for UA-ISFME.

3.6 Real water analysis

The applicability of these procedures to three water samples was evaluated by preconcentrating and then determining the acaricide concentrations. To check the presence of matrix interferences, these samples were spiked with the acaricide standards at concentrations of 10 and 100 ng/mL for both the UA-IL-DLLME and UA-ISFME procedures. Three replicate experiments were performed at each concentration level, and the resultant accuracies and precisions are summarized in Table 2. For the UA-IL-DLLME method, the recoveries for all of the acaricides in the three samples were between 65.9 and 110.0% and had SDs ranging from 0.3–4.8%. For the UA-ISFME method, the recoveries ranged from 25.7–99.4% with SDs between 1.2 and 5.3%. These results demonstrate that real sample matrices had little effect on UA-IL-DLLME with great accuracy and precision of acaricides in water samples. However, the results for UA-ISFME indicated that matrix interferences have an effect on the accuracy of acaricides determination to a certain extent, especially for the determination of pyridaben and spirodiclofen. The different recoveries of acaricides in three water samples can be explained in terms of matrix effect caused by the co-extracted compounds. We are still working on the details of the matrix influence on UA-ISFME in further research. Typical chromatograms obtained from the analytes in sample 3 are shown in Fig. 2 both before spiking with an acaricide concentration of 100 ng/mL and after isolation using both UA-IL-DLLME and UA-ISFME.

3.7 Comparison of the present methods to other methods

Determination of acaricides in water samples by UA-IL-DLLME and UA-ISFME and combined with HPLC–UV is compared to other methods [1, 17, 19–23] such as SPE combined with LC–MS, SPME combined with GC–MS, and liquid-phase microextraction (LPME) combined with GC–μECD in Supporting Information Table S1. As can be seen, the UA-IL-DLLME and UA-ISFME methods both possess lower LOD and shorter extraction times than most of the other methods. Microextractions such as SPME, LPME, and HF-LPME required more time to reach equilibrium. The equilibrium time determines the maximum acaricide concentration that can be preconcentrated and thus affects the sensitivity of the method. However, UA-IL-DLLME and UA-ISFME can reach equilibrium quickly due to the large surface area between the water sample and extraction solvent (IL). Furthermore, the present work does not require special instrumentation. Therefore, UA-IL-DLLME and UA-ISFME are indeed simple, rapid, cheap, easy to use, and environmentally friendly.

4 Conclusions

The combination of UA-IL-DLLME and UA-ISFME with HPLC for the determination of acaricides in water samples was presented. The present work optimized those experimental conditions that affect the extraction efficiency of

Table 2. Recoveries (% ± SD, $n = 3$) for the measurement of acaricides in water samples

	Found (ng/mL)	Sample 1 (ng/mL)		Found (ng/mL)	Sample 2		Found (ng/mL)	Sample 3	
Added (ng/mL)	0	10	100	0	10	100	0	10	100
UA-IL-DLLME									
Clofentezine	ND[a)]	83.6 ± 3.9	77.8 ± 1.4	ND	101.0 ± 2.1	93.9 ± 2.4	ND	96.4 ± 3.5	95.5 ± 2.1
Chlorfenapyr	ND	88.4 ± 3.9	69.7 ± 1.6	ND	77.0 ± 4.7	88.3 ± 3.6	ND	92.0 ± 4.1	94.6 ± 1.7
Fenpyroximate	2.0	80.8 ± 1.9	84.9 ± 4.2	2.1	81.7 ± 3.0	88.9 ± 4.1	1.9	90.8 ± 4.2	95.1 ± 2.2
Diafenthiuron	3.3	89.9 ± 2.2	76.4 ± 4.6	3.2	110.0 ± 3.1	83.4 ± 3.5	3.0	101.7 ± 2.7	84.2 ± 2.2
Pyridaben	1.2	70.1 ± 4.8	65.9 ± 2.7	0.8	82.3 ± 0.1	80.9 ± 3.8	ND	94.2 ± 1.2	84.5 ± 2.4
Spirodiclofen	ND	79.1 ± 0.3	70.3 ± 2.8	ND	85.7 ± 6.4	84.5 ± 3.8	ND	84.2 ± 1.6	85.6 ± 1.9
UA-ISFME									
Clofentezine	ND	96.7 ± 2.7	93.3 ± 2.5	ND	88.7 ± 2.0	90.9 ± 1.2	ND	85.5 ± 1.1	91.4 ± 3.6
Chlorfenapyr	ND	79.0 ± 3.2	79.0 ± 3.4	ND	82.0 ± 5.3	78.8 ± 1.7	ND	71.8 ± 2.9	74.2 ± 3.5
Fenpyroximate	ND	71.7 ± 2.6	71.3 ± 3.8	ND	68.7 ± 5.3	70.0 ± 2.7	ND	69.9 ± 5.5	68.8 ± 2.1
Diafenthiuron	ND	94.5 ± 4.0	71.4 ± 1.4	1.3	94.8 ± 1.8	69.9 ± 2.4	ND	99.4 ± 5.0	70.0 ± 1.8
Pyridaben	ND	58.9 ± 2.2	63.0 ± 4.2	ND	64.7 ± 2.9	62.9 ± 2.1	ND	60.9 ± 4.0	60.4 ± 3.5
Spirodiclofen	ND	41.8 ± 5.0	34.6 ± 4.8	ND	39.8 ± 3.9	34.6 ± 2.4	ND	36.1 ± 3.5	25.7 ± 1.5

a)ND, not detected.

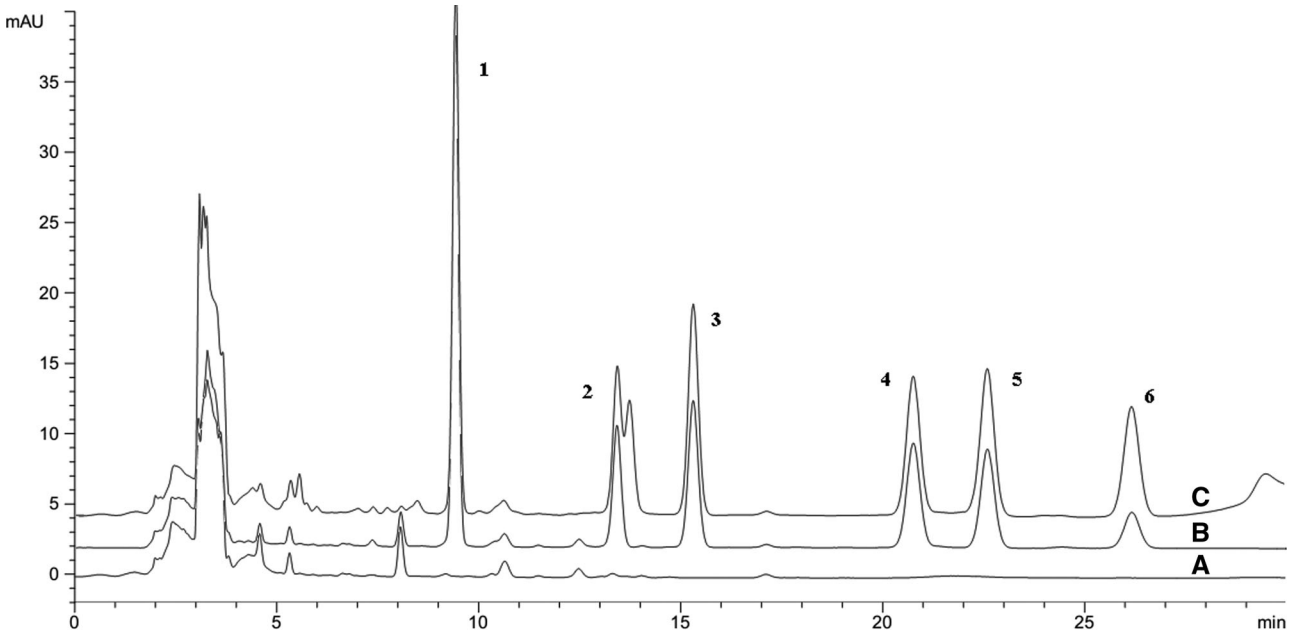

Figure 2. Chromatograms from (A) sample 3 (B) sample 3 spiked with acaricides at a concentration of 100 ng/mL after UA-ISFME and (C) sample 3 spiked with acaricides at each concentration of 100 ng/mL after UA-IL-DLLME. Peak identification: (1) clofentezine, (2) chlorfenapyr, (3) fenpyroximate, (4) diafenthiuron, (5) pyridaben and (6) spirodiclofen.

acaricides from water. After optimization, these methods were analytically characterized in terms of their linearity, precision, sensitivity, and EF. When comparing the validation parameters, UA-ISFME demonstrated more positive characteristics than UA-IL-DLLME for most acaricides (except for spirodiclofen), as observed from the LOD and EF. Finally, both methods were used to determine of acaricides in real water samples. UA-IL-DLLME was successfully used in real samples as expected. However, the determination of selected acaricides in water samples was influenced to some extent using UA-ISFME. Relative to other methods, the present methods have advantages such as simplicity, rapidity, cheapness, and environmental friendliness. In conclusion, the results indicate that UA-IL-DLLME is suitable for determining selected acaricides in real water samples.

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