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Application of dispersion–solidification liquid–liquid microextraction for the determination of triazole fungicides in environmental water samples by high-performance liquid chromatography

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ABSTRACT

A simple, rapid and environmentally friendly method has been developed for the determination of four triazole fungicides (myclobutanil, tebuconazole, triadimenol, hexaconazole) in water samples by dispersion–solidification liquid–liquid microextraction coupled with high performance liquid chromatography-diode array detection. Several variables that affect the extraction efficiencies, including the type and volume of the extraction solvent and dispersive solvent, extraction time, effect of pH and salt addition, were investigated and optimized. Under the optimum conditions, the proposed method is sensitive and shows a good linearity within a range of 0.5–200 ng mL^{-1}, with the correlation coefficients (r) varying from 0.9992 to 0.9998. High enrichment factors were achieved ranging from 190 to 450. The recoveries of the target analytes from water samples at spiking levels of 1.0, 5.0 and 50.0 ng mL^{-1} were between 84.8% and 110.2%. The limits of detection (LODs) for the analytes were ranged in 0.06–0.1 ng mL^{-1}, and the relative standard deviations (RSD) varied from 3.9% to 5.7%. The proposed method has been successfully applied for the determination of the triazole fungicides in real water samples.

1. Introduction

Triazole fungicides are one of the major classes of the pesticides that are widely used in a variety of fruits, vegetables and grain crops [1]. Their characteristics, such as high chemical and photochemical stability, low biodegradability and easy transport in the environment [2], make them persist in soil and water [3]. They have been proven to be endocrine disruptor and considered hazardous to the environment and human health [4]. Monitoring trace levels of these compounds in water has received much attention due to their possible contamination of water resources [5]. According to the European Union Directive, individual pesticide in drinking water must not exceed 0.1 ng mL^{-1} [6]. The high requirements on water quality have resulted in an increasing need for the sensitive analytical methods for the compounds.

Several analytical methods, such as gas chromatography [5,7–12] and high-performance liquid chromatography (HPLC) [12–16], micellar electrokinetic chromatography [17] and thin-layer chromatography [18], have been developed to determine triazole fungicides in water samples. However, a sample enrichment procedure is often needed before the chromatographic analysis because most of the fungicides exist at a trace level in water system.

Generally, liquid–liquid extraction (LLE) [9,19] and solid phase extraction (SPE) [12–13] are widely adopted to extract triazole fungicides from different samples. However, LLE suffers from the disadvantages of being time-consuming and requiring large volumes of samples and toxic organic solvents; SPE techniques typically require reduced amounts of organic solvents relative to LLE, but SPE can still be tedious, time-consuming, relatively expensive, and sometimes suffers from analytes breakthrough when large sample volumes are analyzed. Therefore, much attention is being paid to the development of miniaturized, more efficient and environmentally friendly extraction techniques for the determination of triazole fungicides, such as accelerated solvent extraction (ASE) [20], hollow fiber-based liquid-phase microextraction (HF-LPME) [8,16], solid-phase microextraction (SPME) [10,14], stir-bar sorptive extraction (SBSE) [17], dispersive liquid–liquid microextraction (DLLME) [15].

ASE is a relatively new extraction technique that has been applied successfully in the extraction of some pesticide residues from various matrices. Compared with traditional methods like

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ultrasonic or Soxhlet extraction, it has similar or sometimes even higher extraction efficiencies but consumes less solvent and labor. However, it required a special ASE instrument. In 1999, Pederson-Bjergaard and Rasmussen developed a hollow fiber-based LPME technique (HF-LPME) [21]. In HF-LPME, the micro-extract solvent is contained within the lumen of a porous hollow fiber. This technique can provide high analytes preconcentration and excellent sample cleanup, with the advantage that the fiber is disposable after use due to its low cost. SPME [22] is a simple, organic solvent-free and efficient extraction technique. However, it also suffers from some drawbacks such as sample carry-over, relatively high cost and fiber fragility. SBSE is another solvent-free sample preparation technique based upon sorptive extraction. The most widely used sorptive extraction phase is polydimethylsiloxane (PDMS). At present only PDMS-coated stir-bars are commercially available and this represents one of the main drawbacks of SBSE, since polar compounds are often poorly extracted [23] by PDMS polymer due to its non-polarity. In addition, a long analysis time is often encountered in either SBSE, HF-LPME or SPME. For DLLME, the main drawback is the difficulty to automation and the requirement to use a high-density extraction solvent, such as chlorobenzene, chloroform and carbon tetrachloride, etc., all of which are highly toxic and environmentally unfriendly.

In order to overcome the disadvantages of DLLME, recently, Yamini and co-workers have reported a simple and efficient liquid-phase microextraction method based on the solidification of a floating organic microdrop (LPME-SFO) [24], in which, a less-toxic and low-density extraction solvent with a proper melting point was used. LPME–SFO method has been applied for the analysis of a variety of trace organic pollutants and metal ions in the environmental samples [25–28]. However, the extraction time was somewhat longer in LPME–SFO than that in DLLME, thus it cannot satisfy the demand of fast analysis.

More recently, a new method named dispersive liquid–liquid microextraction based on solidification of floating organic droplet (DLLME-SFO), or dispersion–solidification liquid–liquid microextraction, was introduced by Huang [29,30] and Feng [31]. It is based on DLLME and the solidification of floating organic drop. In this method, the appropriate mixture of an extraction solvent with low-density and proper melting point and a dispersive solvent is rapidly injected into an aqueous sample by syringe. A cloudy solution containing the fine droplets of the extraction solvent dispersed entirely in the aqueous phase is formed, which is attributed to the dipersive role of the dispersive solvent. The analytes in the sample are extracted into the fine droplets, which are further separated by centrifugation. The floated extractant droplet can be collected easily by solidifying it at low temperature. The large contact surface between the sample and the droplets of the extractant speeds up the mass transfer of the analytes. Accordingly, the analysis time can be as fast as DLLME and is shorter than LPME-SFO. The advantages of the dispersion–solidification liquid–liquid microextraction are simplicity of operation, rapidity, low cost, high recovery, compatibility of the extraction solvent with some instrumental analyses and its use of the extraction solvents with lower toxicity in contrast to DLLME.

In this paper, a dispersion–solidification liquid–liquid microextraction followed by high performance liquid chromatography-diode array detection (HPLC-DAD) was investigated for the determination of some triazoles in real water samples. The factors that affect the DLLME-SFO extraction, such as the type of extraction solvent and its volume, the kind and volume of dispersive solvent, sample pH, extraction time and addition of salt, were investigated and optimized. The result reveals that the proposed method is simple, rapid, practical and environmentally friendly.

2. Experimental

2.1. Reagents and materials

Pesticide standards of triazole fungicides (myclobutanil, tebuconazole, triadimenol, hexaconazole) prepared in acetone were purchased from Agricultural Environmental Protection Institution in Tianjin (Tianjin, China). 1-Dodecanol (1-DD-OH), 1-undecanol, *n*-hexadecane (*n*-HD), bromohexadecane were obtained from Beijing Chemical Reagents Company (Beijing, China). Sodium chloride (NaCl), sodium hydroxide (NaOH), acetone, acetonitrile, tetrahydrofuran (THF), ethanol and methanol were from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). The water used throughout the work was double-distilled on a SZ-93 automatic double-distiller purchased from Shanghai Yarong Biochemistry Instrumental Factory (Shanghai, China).

Different water samples, including lake water from shunping (Baoding, China), stream water from Laiyuan (Baoding, China), well water from Wumazhuang (Baoding, China) and all the solvents were filtered through a 0.45-μm membrane to eliminate particulate matters before analysis.

A mixture stock solution containing myclobutanil, tebuconazole, triadimenol and hexaconazole at 10.0 μg mL^{-1} was prepared in methanol. A series of standard solutions were prepared by mixing an appropriate amount of the stock solution with double-distilled water in a 10-mL volumetric flask. All solutions were stored at 4 °C in the dark.

2.2. Instrument

The HPLC system, assembled from modular components (Waters, Milford, MA, USA), consisted of an in-line degasser, a 600E pump, and a diode array detector (DAD). A Millennium^{32} workstation (Waters) was utilized to control the system and for the acquisition and analysis of the data. A Centurysil C_{18} column (4.6 i.d. × 250 mm, 5.0 μm) from Dalian Jiangshen Separation Science Company (Dalian, China) was used for separations. The mobile phase was a mixture of methanol–water (75:25 v/v) at a flow rate of 1 mL min^{-1}. DAD monitoring wavelengths were chosen at 220 nm for all the four triazole fungicides.

2.3. DLLME-SFO procedure

For DLLME-SFO, 10.0 mL water samples and 1.5 g NaCl were placed in a 25 mL screw cap glass test tube. The pH of the sample solution was adjusted to 6.0 by 0.1 mol L^{-1} NaOH. A mixed solution of 12 μL 1-DD-OH (extraction solvent) and 200 μL methanol (dispersive solvent) was rapidly injected into the sample solution, and then the mixture was vortexed for 1 min. A cloudy solution that consists of very fine droplets of 1-DD-OH dispersed into aqueous sample was formed, and the analytes were extracted into the fine droplets. After centrifugation at 3500 r min^{-1} for 3 min, there was a liquid organic droplet floating on the top of the test tube due to its lower density than water. The glass tube was thereafter transferred into an ice bath for 5 min. The solidified organic droplet was transferred into a 500 μL conical vial in which it melted rapidly at room temperature. The extractant was then mixed with 12 μL methanol (because 1-DD-OH cannot soluble well in the mobile phase) and 15 μL of the resultant mixture was injected into the HPLC system for analysis.

2.4. Calculation of enrichment factor (EF)

The EF was defined as the ratio between the analyte concentration in the floated phase ($C_{floated}$) and the initial concentration of the analyte (C_0) in the aqueous sample. In this work, in order to

evaluate the effect of some experimental conditions on the extraction efficiency, the EF was calculated according to the following equation:

$$EF = \frac{C_{final}}{C_0}$$

where EF, C_{final}, and C_0 are the enrichment factor, the final analyte concentration in the mixture solution of the floating extraction solvent and the 12 μL methanol added, and the initial analyte concentration in the aqueous samples, respectively.

3. Results and discussion

In order to obtain the optimum DLLME-SFO conditions for the determination of triazole fungicides in aqueous samples, the influence of different experimental parameters including the type and volume of the extraction solvent and dispersive solvent, extraction time, sample pH and the presence of salt on the performance of DLLME-SFO were investigated.

In the experiment, 10.0 mL of double-distilled water spiked with 10.0 ng mL^{-1} each of the four triazole fungicides was used to study the extraction performance under different experimental conditions. All the experiments were performed in triplicate and the means of the results were used for optimization.

3.1. Selection of extraction and dispersive solvent

Regarding the DLLME-SFO process, the selection of an appropriate extraction solvent is limited by several factors, such as it should have low solubility in water, low melting point near room temperature (in the range of 10–30 °C), lower density than water, high affinity to analytes, low volatility and good chromatographic behavior. Based on these criteria, 1-dodecanol (1-DD-OH), 1-undecanol, *n*-hexadecane (*n*-HD), and bromohexadecane were investigated for the extraction of the target fungicides. On the other hand, dispersive solvent is also of great importance for the establishment of an efficient DLLME-SFO process. In the DLLME-SFO method, dispersive solvent should be miscible with both water and the extraction solvents and could form a cloudy state when injected with the extractant into water. For this purpose, different solvents, i.e., acetone, methanol, ethanol, acetonitrile and THF were considered as potential dispersive solvents. Due to a limited number of organic extractants, all combinations of using 1-DD-OH, *n*-HD, 1-undecanol, bromohexadecane as extractant with acetone, methanol, ethanol, acetonitrile and THF as dispersive solvent were investigated. The results indicate that the chromatographic peak of THF interfered with the analysis of the target analyte (myclobutanil). *n*-HD and bromohexadecane cannot be dissolved in the above five dispersive solvents possibly due to their strong hydrophobicity. For 1-DD-OH and 1-undecanol, their solubility in acetonitrile was not so good as to form a homogeneous phase. On the other hand, 1-DD-OH and 1-undecanol gave a similar extraction efficiency for the analytes and the highest extraction efficiency was obtained when methanol was used as dispersive solvent. Considering that 1-undecanol is more expensive than 1-DD-OH, and needs a longer time for the solidification process since the melting point of 1-undecanol (15 °C) is lower than that of 1-DD-OH (24 °C), 1-DD-OH and methanol were selected as extraction solvent and dispersive solvent in subsequent experiments.

3.2. Effect of extraction solvent volume

To examine the effect of the extraction solvent volume on the extraction efficiency for the analytes of interest, different volumes of 1-DD-OH (10.0, 12.0, 15.0, 20.0 and 25.0 μL) with a constant volume of the dispersive solvent methanol (200 μL) were investigated.

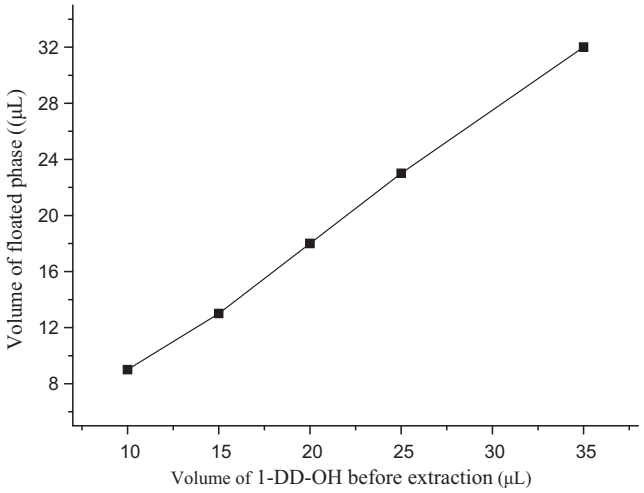

Fig. 1. Effect of the volume of injected extraction solvent on the volume of floated phase obtained from DLLME-SFO.

As shown in Figs. 1 and 2, by increasing the volume of 1-DD-OH, the volume of the resultant floating phase was increased while the peak areas decreased, which may be because the concentration of the analytes in the floating phase was slightly decreased due to the dilution effect [31]. In addition, although the use of lower volumes of 1-DD-OH (<12 μL) could result in a higher enrichment factor, however, the resultant volume of the extractant was too small for the subsequent experimental manipulations. For this reason, 12 μL 1-DD-OH was chosen for the studies.

3.3. Effect of dispersive solvent volume

To study the effect of the volume of the dispersive solvent on the performance of the presented method, various volumes of methanol in the range of 100–800 μL with 12 μL 1-DD-OH as extraction solvent were investigated. Fig. 3 illustrates the variations of the peak areas of the triazole fungicides versus the volume of the dispersive solvent. As can be seen in Fig. 3, there is a maximum extraction efficiency at 200 μL. The reason for this could be that at a lower volume of methanol than 200 μL, a cloudy state could not be formed well, therefore, resulting in a low peak area; on the other hand, when the volume of methanol was higher than 200 μL, the solubility of the fungicides in water was increased, thus giving

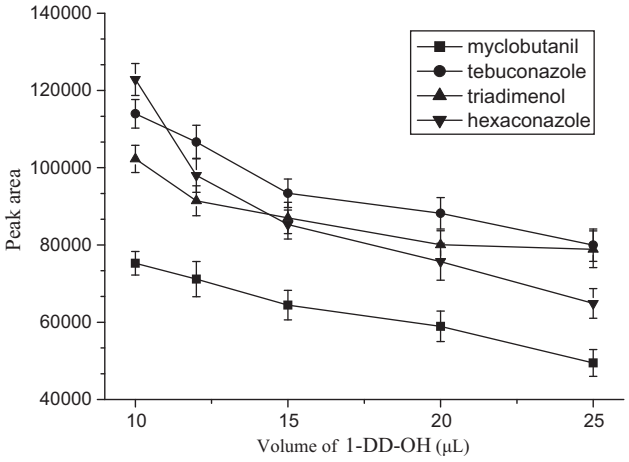

Fig. 2. Effect of the volume of extraction solvent (1-DD-OH) on the relative peak area. Extraction conditions: sample volume, 10.0 mL; extraction solvent, 1-DD-OH; dispersive solvent, 200 μL methanol.

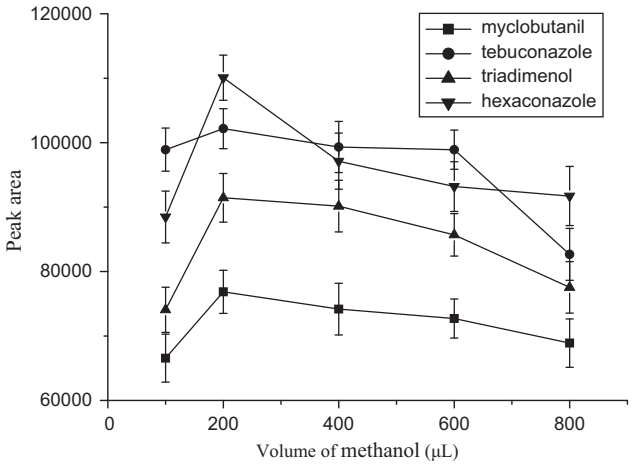

Fig. 3. Effect of the volume of dispersive solvent (methanol) on the relative peak area. Extraction conditions: sample volume, 10.0 mL; extraction solvent, 12 μL 1-DD-OH; dispersive solvent, methanol.

a decresed peak area. Therefore, 200 μL methanol was selected as the optimal dispersive solvent volume.

3.4. Effect of extraction time

Extraction time is one of the most important factors in most extraction procedures. In DLLME-SFO, the extraction time was defined as the time interval elapsed between the addition of the mixture of the extraction solvent and dispersive solvent to the sample and the time before centrifugation. For the present study, the effect of the extraction time was studied over the time range between 1 and 10 min. As a result, the influence of the extraction time on peak area was not remarkable. This is because the equilibrium state can be achieved quickly and therefore the extraction time required can be very short in DLLME-SFO. The short extraction time is one of the remarkable advantages of the DLLME-SFO technique. Consequently, 1 min of extraction time was chosen in the following experiments.

3.5. Effect of sample pH

Sample pH can also play an important role in the extraction process. The influence of sample pH on the extraction efficiency was tested in the range of 2–10. The results (Fig. 4) demonstrated that the best extraction efficiencies for each target analyte were obtained when the sample pH was 6, which is in agreement with the literature method [32,12]. This result may be due to that the target compounds were stable in neutral and weak acidic media, and they were unstable in alkaline media and could be ionized in relatively strong acidic media. Thereby, the pH of the sample solution was adjusted to 6.

3.6. Effect of salt addition

The ionic strength affects the partitioning coefficients of analytes between the aqueous and organic phases. The effect of salt concentration on the extraction efficiency was studied over the sodium chloride concentration range from 0% to 20% (w/v). As is shown in Fig. 5, the peak area of the triazole fungicides was increased with the increase of the salt concentration up to 15%. However, at the salt concentration higher than 15%, the peak area of the triazoles remained almost constant and the NaCl could precipitated in the solidified solvent phase, which could result in a fast HPLC column degradation. Hence, 15% NaCl was added in all the subsequent experiments.

Under the above optimized experimental conditions, the enrichment factors of DLLME-SFO for myclobutanil, tebuconazole, triadimenol and hexaconazole were between 190 and 450.

3.7. Application of DLLME-SFO in water samples

3.7.1. Linearity, repeatability and limits of detection (LODs)

Important parameters such as linearity, LODs and precision were determined to evaluate the method performance. A series of working solution containing each of the four triazoles at seven concentration levels of 0.5, 5.0, 20.0, 50.0, 100.0, 150.0 and 200.0 ng mL^{-1} were prepared for the establishment of the calibration curve. For each level, five replicate experiments were performed. As shown in Table 1, the linear response was observed in the range of 0.5–200 ng mL^{-1}, with the correlation coefficient (r) ranging from 0.9992 to 0.9998. The LODs ($S/N = 3$) of the four triazole fungicides were ranged in 0.06–0.1 ng mL^{-1}. The limits of quantification (LOQs, $S/N = 10$) were ranged in 0.2–0.33 ng mL^{-1}. The repeatability study was carried out by extracting the spiked water samples at the concentration of each triazoles at 2.0 and 20 ng mL^{-1}, and the relative standard deviations (RSDs) varied from 3.9% to 5.7%.

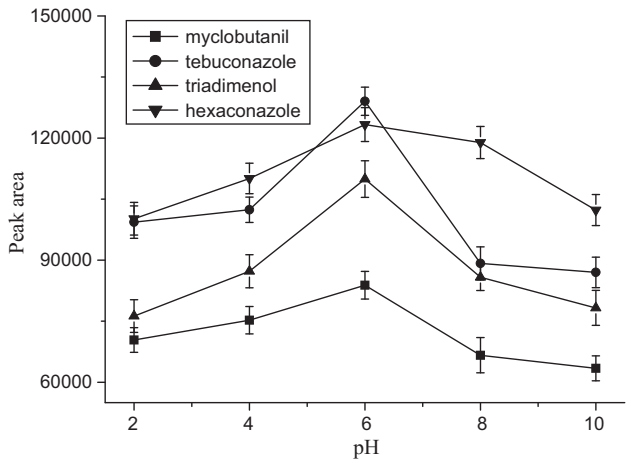

Fig. 4. Effect of sample pH on the relative peak area. Extraction conditions: sample volume, 10.0 mL; extraction solvent, 12 μL 1-DD-OH; dispersive solvent, 200 μL methanol.

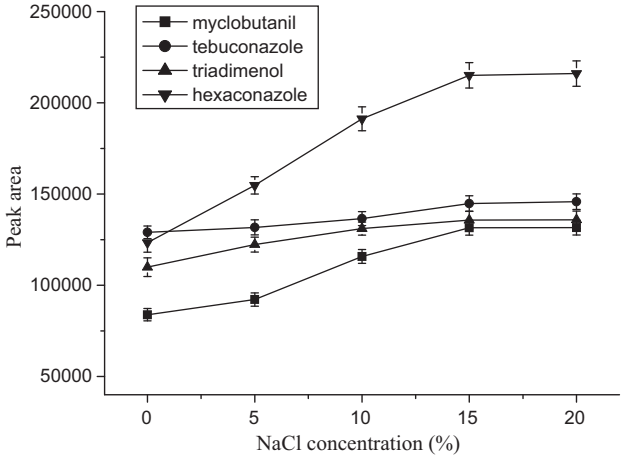

Fig. 5. Effect of salt addition on the relative peak area. Extraction conditions: sample volume, 10.0 mL; extraction solvent, 12 μL 1-DD-OH; dispersive solvent, 200 μL methanol; sample pH, 6.

Table 1
Analytical performance data for the triazole fungicides by the DLLME-SFO method.

Triazoles	LR[a] (ng mL^{-1})	r	RSD (%) (n = 5)	EF	LOD (ng mL^{-1})	LOQ (ng mL^{-1})
Myclobutanil	0.5–200	0.9995	4.3	289	0.1	0.33
Tebuconazole	0.5–200	0.9996	5.7	190	0.08	0.26
Triadimenol	0.5–200	0.9992	3.9	201	0.08	0.26
Hexaconazole	0.5–200	0.9998	4.6	450	0.06	0.2

[a] LR, linear range.

Table 2
Determination of triazoles residues and recoveries in lake, well and stream water samples.

Triazoles	Spiked (ng mL^{-1})	Lake water (n = 5)			Well water (n = 5)			Stream water (n = 5)		
		Measured (ng mL^{-1})	R[b] (%)	RSD (%)	Measured (ng mL^{-1})	R[b] (%)	RSD (%)	Measured (ng mL^{-1})	R[b] (%)	RSD (%)
Myclobutanil	0	nd[a]			nd[a]			nd[a]		
	1.0	0.86	86.0	5.2	0.88	88.0	5.5	0.90	90.0	5.0
	5.0	4.38	87.6	4.1	5.51	110.2	5.0	4.59	91.8	5.2
	50.0	45.2	90.4	4.4	46.4	92.8	3.9	48.1	96.2	4.5
Tebuconazole	0	nd[a]			nd[a]			2.18		4.6
	1.0	0.87	87.0	4.9	0.90	90.0	5.1	2.98	90.0	5.4
	5.0	4.81	95.2	4.3	4.30	86.0	4.0	7.06	97.6	4.9
	50.0	47.2	94.4	5.6	44.9	89.8	5.4	50.08	95.8	4.2
Triadimenol	0	nd[a]			nd[a]			nd[a]		
	1.0	0.85	85.0	5.8	0.86	86.0	6.0	0.87	87.0	5.7
	5.0	5.07	101.4	3.8	4.31	86.2	4.5	4.58	91.6	3.5
	50.0	42.4	84.8	4.0	44.2	88.4	4.6	44.9	89.8	6.1
Hexaconazole	0	nd[a]			nd[a]			nd[a]		
	1.0	0.87	87.0	4.9	0.91	91.0	5.4	0.89	89.0	5.6
	5.0	4.97	99.4	4.7	4.73	94.6	3.7	4.28	85.6	4.0
	50.0	46.3	92.6	4.9	49.4	98.8	5.4	43.5	87.0	5.1

[a] nd, not detected.
[b] R, recovery of the method.

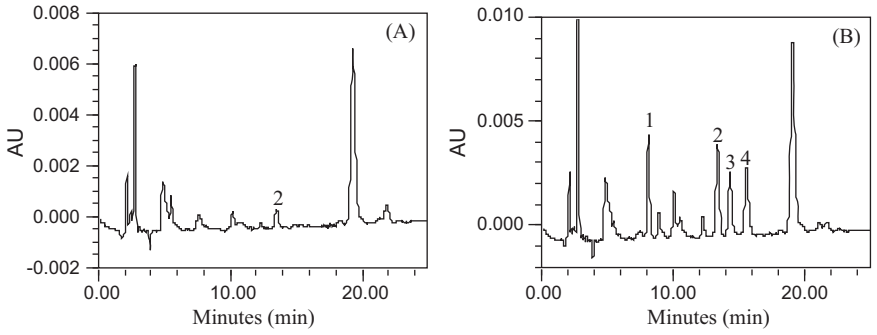

Fig. 6. The typical chromatograms of (A) stream water sample and (B) stream water sample spiked with triazole fungicides at each concentration of 5.0 ng mL^{-1} (220 nm). Peak identification: (1) myclobutanil, (2) tebuconazole, (3) triadimenol, (4) hexaconazole.

3.7.2. *Water samples analysis*

DLLME-SFO-HPLC was applied for the determination of the four triazoles in real water samples, including lake, well and stream water. Only tebuconazole was found in stream water at a concentration of 2.18 ng mL^{-1}.

For the recovery experiment, water samples were spiked with the standards of the four triazoles at the concentration of 1.0, 5.0 and 50.0 ng mL^{-1}, respectively. The results are summarized in Table 2, which exhibited that the recoveries for the studied triazole fungicides were between 84.8% and 110.2%. Fig. 6A and B shows the typical chromatograms of the extracted fungicides from stream water before and after being spiked at 5 ng mL^{-1} of each of the four triazoles.

Table 3
Comparison of the current DLLME-SFO method with other sample preparation techniques for the determination of the triazoles.

Methods	Linearity (ng mL^{-1})	LOD (ng mL^{-1})	Extraction time (min)	RSD (%)	References
SPE–HPLC–MS^2	–	0.0004–0.0005	85	9.2–12	[12]
SPME–HPLC–DAD	20–250	27	30	9.2–18.1	[14]
CSM–LPME–micro-LC-UV	2.0–100	1	20	6.5	[32]
HF–LPME–UHPLC[a]–MS^2	5–100	1	45	4.5–11.5	[16]
IL–DLLME[b]–HPLC–DAD	122–6830	3.86	<1	2.5–5	[15]
DLLME–SFO–HPLC–DAD	0.5–200	0.06–0.1	1	3.9–5.7	This method

[a] UHPLC, ultra-high pressure liquid chromatography.
[b] IL-DLLME, ionic liquid based dispersive liquid–liquid microextraction.

3.8. Comparison of DLLME-SFO with other sample preparation techniques

The performance of the proposed DLLME-SFO method was compared with other reported methods such as DLLME, HF-LPME, cone-shaped membrane liquid phase microextraction (CSM-LPME), SPE and SPME. As listed in Table 3, the DLLME-SFO-HPLC-DAD method has comparable LODs with other methods except SPE-HPLC-MS^2. HF-LPME, CSM-LPME, SPE and SPME required a longer time for equilibrium to be established than that for DLLME and DLLME-SFO, which can reach the equilibrium extremely quickly due to the large surface area between the extraction solvent and the sample solution. In comparison with DLLME, lower toxicity extracting solvents was used in DLLME-SFO. Additionally, no specific holders such as the needle tip of microsyringe, hollow fiber or membrane is required for supporting the organic microdrop.

4. Conclusions

In the present study, dispersion–solidification liquid–liquid microextraction coupled with HPLC-DAD detection illustrates a simple and sensitive approach for the extraction and determination of some triazole fungicides in water samples. It combined the advantages of both DLLME and LPME-SFO such as rapid, low cost, efficient, environmentally friendly and easy to operate. The DLLME-SFO method has been successfully applied to the analysis of triazole fungicides in water samples with good repeatability and LODs, indicating that the proposed method is suitable for the determination of the triazole fungicides in real water samples.

Acknowledgments

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