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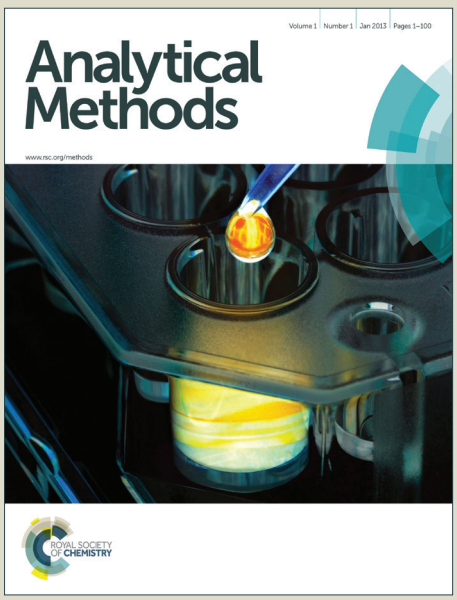

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Microwave-assisted liquid-liquid microextraction based on solidification of floating organic droplet for the determination of triazines in honey samples

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Mingzhu Hu[a], Lijie Wu[a], Ying Song[a], Zhanchao Li[a], Qiang Ma[b], Hanqi Zhang[a], Ziming Wang[a] *

Microwave-assisted liquid-liquid microextraction based on solidification of floating organic droplet (MA-LLME-SFO) was first developed and applied to the extraction of triazines in honey samples. 1-Dodecanol, which is of low toxicity, low density and proper melting point near room temperature, was chosen as the extraction solvent. Furthermore, traditional organic dispersive solvents were avoided in this method with the aid of the microwave irradiation. Several experimental parameters, including type and volume of extraction solvent, microwave power and irradiation time, pH of sample solution, ionic strength and centrifugation rate were investigated and optimized. The proposed method showed a good linearity within the range of 5.00-250.00 μg/kg with the correlation coefficients ranging from 0.9994 to 0.9998. The limits of detection for cyanazine, desmetryn, terbuthylazine and dimethametryn were 1.39, 0.95, 1.20, and 1.07 μg/kg, respectively. The recoveries of the analytes ranged from 74.84 to 112.74% and relative standard deviations were lower than 13.10%, when the present method was applied to the analysis of real samples.

1. Introduction

Triazine herbicides are widely used in the field of agriculture due to their high power for weed control. However, the triazine herbicides and its degradations remain unchanged in the environment during a long period of time,[1] which could lead to cancer, birth defects and interruption of hormone functions.[2] Because of the extended and widespread use, the residues of the herbicides have been found in most agriculture products.[3, 4] In recent years, the consumption of honey has increased considerably benefiting from its high nutrition and good taste. However, the bees, gathering nectar and pollen from contaminated blossom and often coming in contact with contaminated surfaces and plants, can introduce the herbicides into honey.[1] Consequently, there is an urgent necessity to detect triazine herbicides in honey to guarantee public health and safety.

Many methods have been reported for determining trazines including high-performance liquid chromatography (HPLC),[5] capillary liquid chromatography,[6] liquid chromatography-mass spectrometry (LC-MS)[7] and gas chromatography-mass spectrometry (GC-MS).[8] Considering the matrix complexity of the samples and the low concentration of the herbicides, sample preparation plays an important role in the whole analytical procedure. Liquid-liquid extraction (LLE)[9] and solid phase extraction (SPE)[10] have been applied for extraction and preconcentration of herbicides from the matrix. The LLE are general extraction techniques used in the case of complex matrix samples with the disadvantage of highly time-consuming, labor intense and long exposure of laboratory personnel to harmful vapors from chemical reagents, particularly organic solvents.[11] The conventional SPE usually was applied to aqueous solutions to make targets adsorb onto sorbent in cleanup procedures. Therefore, an evaporation or dilution of extract usually is needed for SPE.[10, 12] One of the latest trends in analytical chemistry is approached toward the simplification of sample preparation.[13] Some microextraction methods were developed widely in recent years including the solid-phase microextraction (SPME)[14] and liquid-phase microextraction (LPME).[15] SPME is a solvent-free process developed by Arthur and Pawliszyn[16] that extract and preconcentrate analytes simultaneously with expensive, fragile and short-life fiber. LPME including single-drop microextraction (SDME)[17] and hollow fiber liquid-phase microextraction (HF-LPME)[18] is inexpensive and minimal exposure to toxic organic solvents. However, the small contact surface area of the drop or fiber limits its application, so a long extraction time is unavoidable.

To resolve the problems, in 2006, Rezaee et al.[19] developed dispersive liquid-liquid microextraction (DLLME) by injecting extraction solvent and disperser solvent into aqueous sample to form cloudy state. The increasing contact surface between phases reduces the extraction time and enhances enrichment factors. However, the toxic and environmentally hazardous extraction solvents are applied through the process, such as chlorobenze, chloroform, and carbon tetrachloride.[20] Another challenge is to enhance the dispersion of the extraction solvent in the aqueous sample phase, the water-miscible organic dispersive solvent is required in DLLME. But the partition coefficient of analytes into the extraction solvent will

[a] College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China.
[b] Chinese Academy of Inspection and Quarantine, Beijing 100123, China.
† Footnotes relating to the title and/or authors should appear here.
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decrease due to the existence of dispersive solvent.[21, 22] Ultrasound-assisted emulsification microextraction (USAEME)[23] makes a water-immiscible extraction solvent disperse into a sample aqueous solution by ultrasound-assisted emulsification without using any dispersive solvent. But the process is still time-consuming than DLLME. Hence, it is necessary to develop a novel method overcoming these demerits such as the use of high volume toxic organic solvents, the loss of analytes in dispersive solvent and long extraction time. Dispersive liquid-liquid microextraction based on solidification of floating organic droplet (DLLME-SFO) [24] uses extraction solvents with low density and relatively high melting point. After freezing, the floating extraction solvent solidifies and can be collected easily. However, the use of traditional organic dispersive solvents to enhance the recoveries or reduce the extraction time is inevitable.

Microwave-assisted extraction (MAE) is a rapid and effective extraction technique compared to traditional extraction techniques and has been applied to extract biologically active compounds from different matrices.[25] The microwave-assisted dispersive liquid-liquid microextraction (MA-DLLME) has been successfully applied for the preconcentration of uranium from water samples.[26] Contrast to the conventional extraction methods, microwave assisted extraction greatly reduces the extraction time and enhances the recoveries.

In this paper, in order to simplify the analytical step, avoid the use of toxic solvents and enhance the sensitivity, MA-LLME-SFO was first developed to extract triazines in honey samples. This method combines the advantages of MA-LLME with DLLME-SFO. Unlike traditional DLLME or DLLME-SFO, the extract solvent disperses into the sample solution with the aid of microwave irradiation instead of the dispersive solvent. After heating a few seconds by microwave, the high temperature of the sample solution contributed to the solubility of the extraction solvent (1-dodecanol) into the water, and accelerated the extraction process of the analytes into the microdroplet in a relatively short time. After freezing, the solidified droplet can be easily collected. Detailed effects of various experimental parameters were investigated. To the best of our knowledge, this work first applied MA-LLME-SFO to determine pesticides in honey samples.

2. Experimental

2.1 Chemicals and reagents

Cyanazine, desmetryn, terbuthylazine and dimethametryn were obtained from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Standard stock solutions for the herbicides at the concentration level of 500 μg/mL were prepared in acetonitrile and stored at 4 °C. The mixed working solutions were obtained by diluting the standard stock solutions with acetonitrile or pure water. Chromatographic grade acetonitrile and methanol were purchased from Fisher Scientific Company (Pittsburgh, PA, USA). Pure water was obtained with a Milli-Q water purification system (Millipore Co., USA). Sodium chloride, sodium hydroxide, hydrochloric acid and 1-dodecanol were of analytical-reagent grade and purchased from Beijing Chemical Factory (Beijing, China). 1-undecanol (98%) and 1-tetradecanol (95%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China).

2.2 Apparatus and instruments

Chromatographic separation and determination of the herbicides were performed on the 1100 series liquid chromatograph (Agilent Technologies Inc., USA) equipped with quaternary gradient pump, a degasser, photodiode-array detector (DAD), a heated column compartment, an injection value, and a LC workstation. Eclipse XDB-C18 column (3.5 μm, 4.6 mm × 150 mm, Agilent, USA) was used.
The extraction was performed on a modified household microwave oven (SANYO, China) with a maximum microwave output power of 600 W. The microwave output power can be controlled with a continuously changeable transformer. A DELTA-320 acidity meter (Mettler-Toledo Instruments, Shanghai, China) was used for pH measurement. The phase separation was performed on a LDZ4-1.2 centrifuge (Jingli centrifuge, Beijing, China).

2.3 Sample preparation

Four honey samples were purchased from a local supermarket (Changchun, China), including one kind of locust honey (sample 1), one kind of linden honey (sample 2) and two kinds of medlar honey (samples 3 and 4). 2.0 g of honey was weighed and added into a 10 mL of centrifugal tube, and then 10 mL of water was added and the mixture was vortexed until a homogeneous sample solution was obtained. The sample solution was filtered through 0.45 μm filters before extraction.

The samples used for recovery and precision studies were previously determined to be free of the pesticides considered. The spiked samples were prepared by spiking the mixed working standard solution into samples. All results were obtained with sample 1 except for those mentioned in Sections 3.2.4.

2.4 Extraction procedure

The homogeneous sample solution was placed into a 10 mL glass centrifuge tube and adjusted with NaOH solution to pH 5. Then, 70 μL 1-dodecanol as extraction solvent was added into the sample solution. The tube was immediately placed in the microwave oven and irradiated under the microwave power of 300 W for 40 s. Then the mixture was shaken by hand for 20 s, the analytes transferred into the extraction droplet in a relatively short time. After centrifugation at 3500 rpm for 3 min, the 1-dodecanol droplet floated at the top of the tube for its low density. The test tube was thereafter put into an ice bath for 5 min, and the droplet solidified due to the low melting point. After transferred into a conical vial, the melt 1-dodecanol was diluted to 200 μL with methanol for HPLC analysis.

2.5 Chromatographic determination

A gradient elution solvent was applied which contained water as mobile phase A and acetonitrile as mobile phase B. The gradient condition was as follows: 0-8 min, 45-50% B; 8-10 min, 50-60% B; 10-17 min, 60% B; 17-18 min, 60-70% B; 18-22 min, 70% B; 22-24 min, 70-45% B. The flow rate of the mobile phase was 0.5 mL/min and the temperature of the column was kept at 35 °C. The injection

volume of analytical solution was 20 µL. The monitored wavelength was 228 nm for the trazines.[27]

3. Results and discussion

3.1 Optimization of extraction

3.1.1 Type of extraction solvent

An appropriate extraction solvent is of great importance to the extraction efficiency. The extraction solvent should meet the following requirements: it should have a lower density than water, a low solubility in water and melting point near the room temperature. Generally, 1-undecanol, 1-dodecanol and 1-tetradecanol have been recommended. Fig. 1 showed that extraction efficiency of 1-undecanol and 1-dodecanol was similar. However, the solidification of 1-dodecanol was faster for its higher melting point (24 °C) than 1-undecanol (15 °C). Therefore, 1-dodecanol was selected for further studies.

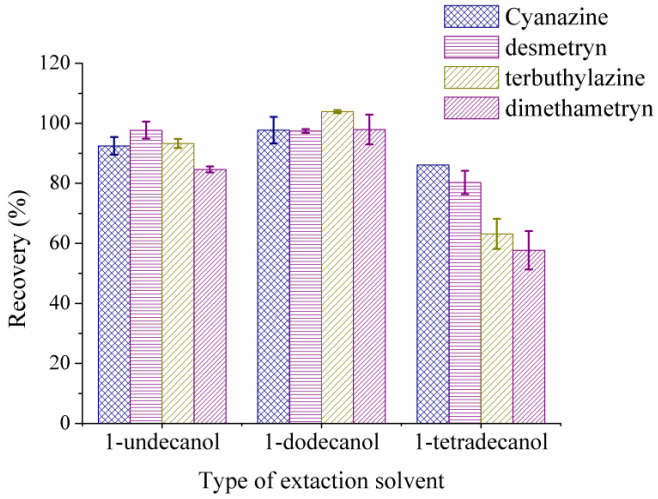

Fig. 1 The effect of extraction solvent on the extraction recovery of triazines. Experimental condition: the volume of extraction solvent, 70 µL; microwave power, 300 W; microwave irradiation time, 40 s; pH of the sample solution, 5; NaCl concentration, 0%; centrifugation rate 3500 rpm; spiked sample 1 (locust honey) at 90 µg/kg.

3.1.2 Effect of volume of extraction solvent

In order to study the effect of extraction solvent volume on the extraction efficiency, the volume of 1-dodecanol was varied in the range from 30 to 80 µL, and the results were shown in Fig. 2. The extraction efficiency increased correspondingly with the increase of the volume from 30 to 70 µL, because diffusion rate of the analytes from the solution into microdrop is directly related to the interfacial area between the two liquid phases. When the volume exceeded 70 µL, the increase of the recoveries was not obvious. Hence, 70 µL of 1-dodecanol was chosen in the proposed method.

3.1.3 Effect of microwave power

The effect of microwave power on the recoveries of triazines was studied by varying the power between 60 and 360 W when the irradiation time was 40 s. As observed in Fig. 3, the recoveries of triazines increased with the increase of microwave power from 60 to 300 W, and slowly decreased thereafter. The temperature can affect both the mass transfer rates of analytes and the contact area between 1-dodecanol and aqueous solution.[28] Furthermore, the temperature of sample solution was related to the microwave power and irradiation time. When the microwave power was too low, the 1-dodecanol was not dispersed well resulting in a relatively low amount of analytes transferring into the droplet. But the high microwave power may also contribute to the degradation of the analytes.[29, 30] The main decomposition reaction of triazines should be the hydrolysis.[31] Thus, 300 W of microwave power was selected.

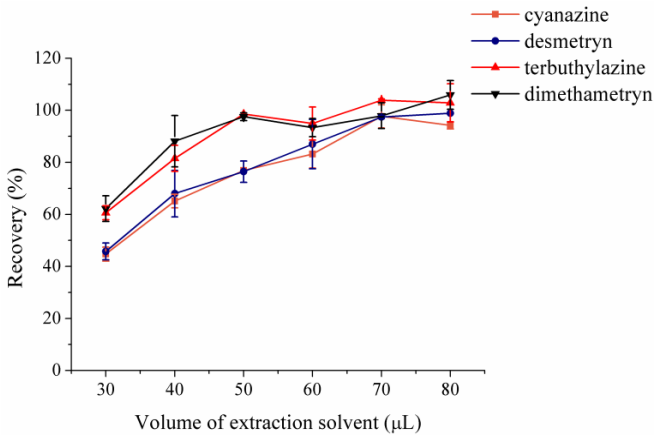

Fig. 2 The effect of volume of extraction solvent on the extraction recovery of triazines. Experimental condition: the extraction solvent, 1-dodecanol; microwave power, 300 W; microwave irradiation time, 40 s; pH of the sample solution, 5; NaCl concentration, 0%; centrifugation rate 3500 rpm; spiked sample 1 (locust honey) at 90 µg/kg.

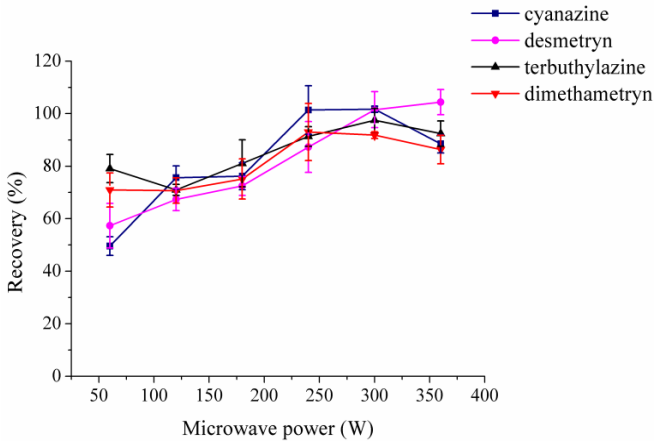

Fig. 3 The effect of microwave power on the extraction recovery of triazines. Experimental condition: the extraction solvent, 1-dodecanol, 70 µL; microwave irradiation time, 40 s; pH of the sample solution, 5; NaCl concentration, 0%; centrifugation rate 3500 rpm; spiked sample 1 (locust honey) at 90 µg/kg.

3.1.4 Effect of microwave irradiation time

The effect of irradiation time ranging from 0 to 80 s was studied under 300 W of microwave power. As shown in Fig. 4, the recoveries of the target analytes increased gradually with the increase of microwave irradiation time from 0 to 40 s, and then decreased when the time exceeds 40 s. Too high temperature caused by long irradiation time may result in the degradation of the analytes.[29, 30] Most of the recoveries of trazines were the highest when the extraction time was 40 s. Thus, 40 s was considered as the appropriate extraction time.

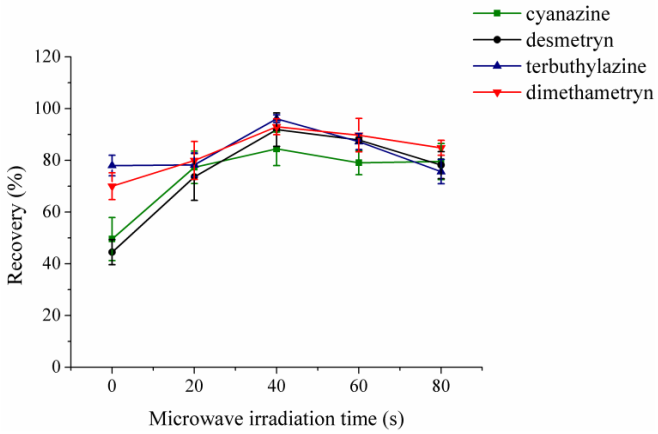

Fig. 4 The effect of microwave irradiation time on the extraction recovery of triazines. Experimental condition: the extraction solvent, 1-dodecanol, 70 μL; microwave power, 300 W; pH of the sample solution, 5; NaCl concentration, 0%; centrifugation rate 3500 rpm; spiked sample 1 (locust honey) at 90 μg/kg.

3.1.5 Effect of pH of sample solution

The pH of sample solution plays an important role in the extraction of analytes. When the neutral form of the target analytes prevails, the maximum extraction efficiency will be achieved.[32] Therefore, the effect of pH values ranging from 2.0 to 8.0 was investigated. Triazines are ionisable compounds (the pKa values for cyanazine, desmetryn, terbuthylazine and dimethametryn were 1.6, 3.93, 1.94 and 3.69, respectively). It can be seen from Fig. 5 that the extraction efficiency greatly increased when the pH was changed from 2 to 5, then slightly decreased after pH of 5.0. We think the proper reason was that the triazines would change in netural forms when pH increased from 2 to 5;[33, 34] on the other hand, they could be easily hydrolyzed in strong acid or alkali environment at high temperature.[35] Hence, pH 5.0 was chosen in the following experiments.

3.1.6 Effect of ionic strength

The addition of salt to the extract is usually made to improve the enrichment efficiency of the analytes, because the increased ionic strength of aqueous phase could aid the partition of analyte to organic phase.[36] To examine the influence of ionic strength on the extraction efficiency, a series of experiments were performed by adding different amount of sodium chloride (0-10%, w/v). Fig. 6 showed the effect of ionic strength on the extraction recoveries. For dimethametryn and terbuthylazine, extraction efficiency was decreased with the increasement of NaCl, which was expected as salting-in effect.[37] In this case, the addition of salt increased the viscosity of the solution, which inhibited the mass transfer rate in extraction process. Subsequently, the amount of analytes transferring into the floating phase decreased, which resulted in the decreasement of the peak area of analytes. For cyanazine and desmetryn, the recoveries remain constantly or increase slightly, respectively. Therefore, salt was not added to the aqueous samples in the proposed method.

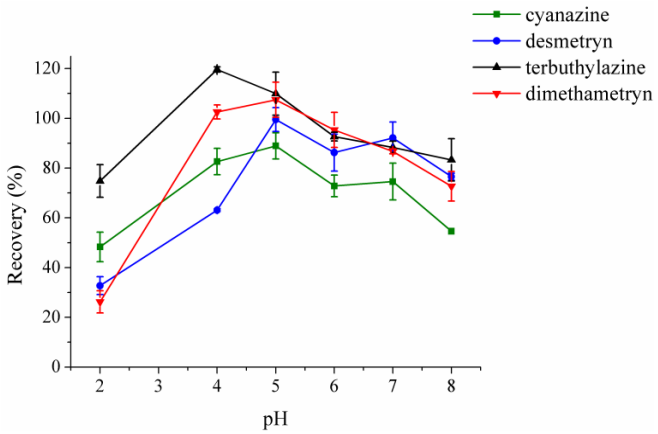

Fig. 5 The effect of pH of sample solution on the extraction recovery of triazines. Experimental condition: the extraction solvent, 1-dodecanol, 70 μL; microwave power, 300 W; microwave irradiation time, 40 s; NaCl concentration, 0%; centrifugation rate 3500 rpm; spiked sample 1 (locust honey) at 90 μg/kg.

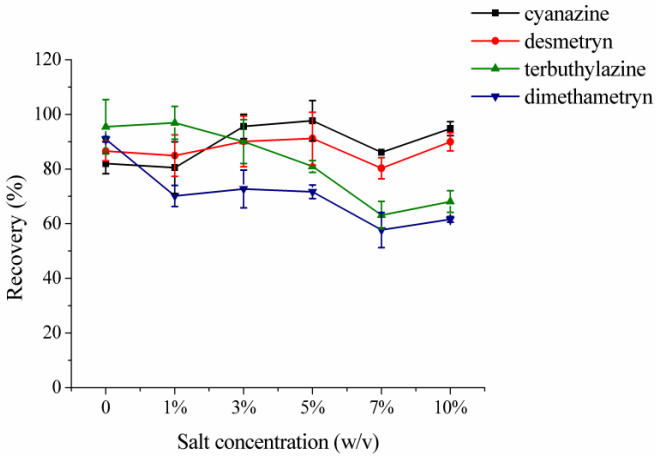

Fig. 6 The effect of ionic strength on the extraction recovery of triazines. Experimental condition: the extraction solvent, 1-dodecanol, 70 μL; microwave power, 300 W; microwave irradiation time, 40 s; pH of the sample solution, 5; centrifugation rate 3500 rpm; spiked sample 1 (locust honey) at 90 μg/kg.

Table 1 Analytical performance

Analyte	Regression equation[a)]	Correlation coefficient	Liner range (μg/kg)	LOD (μg/kg)	LOQ (μg/kg)	Intraday (n=5)		Interday(n=5)	
						Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Cyanazine	A=0.5151c+1.2140	0.9995	5.00-250	1.39	4.63	88.23	5.58	85.29	6.17
Desmetryn	A=1.1476c-3.9705	0.9998	5.00-250	0.95	3.15	92.85	5.70	92.75	5.27
Terbuthylazine	A=1.5697c+0.2608	0.9995	5.00-250	1.20	3.99	100.71	5.22	96.45	3.93
Dimethametryn	A=1.6165c-2.0380	0.9994	5.00-250	1.07	3.20	97.90	6.60	95.10	4.71

a) A, peak area of triazines; c, trazines concentration in μg/kg

Table 2 Analytical results of real samples (n=3)

Analyte	Spiked (μg/kg)	Sample 1		Sample 2		Sample 3		Sample 4	
		Recovery (%)	RSD %	Recovery (%)	RSD %	Recovery (%)	RSD %	Recovery (%)	RSD %
Cyanazine	10	98.11	10.70	112.74	4.27	98.74	6.46	88.99	3.79
	100	80.33	5.94	83.87	5.75	91.65	5.21	83.30	3.58
Desmetryn	10	90.53	8.25	83.73	3.89	109.60	9.98	97.87	3.87
	100	82.70	4.20	91.59	1.50	82.70	4.61	86.58	2.57
Terbuthylazine	10	83.02	7.46	74.84	13.10	76.10	2.93	83.02	8.37
	100	81.10	2.40	91.08	5.24	78.98	6.45	87.90	6.35
Dimethametryn	10	75.89	4.07	107.09	8.60	83.69	4.24	75.89	4.23
	100	84.38	2.61	101.88	6.57	78.12	4.87	81.25	4.25

Table 3 Comparison with other reported methods for the triazine herbicides determination in liquid samples

Method	Matrix	Type and volume of extraction solvent	Dispersant/ emulsifier	Extraction time(min)	Recovery (%)	LOD (μg/kg)	Ref.
DLLME-HPLC-UV	Honey	175 μL $[C_6MIM][PF_6]$	50μL 10% Triton X 114	10	60.1–133	5.31–8.59[a]	21
DLLME-GC-MS	Water	12.0μL chlorobenzene	1.00mL acetone	5	85.2-119.4	0.021-0.12[b]	8
SPE-HPLC-UV	Water	5 mL ethanol (elution solvent)	-	-	69.2-95.4	3.2-8.6[b]	10
HF-LPME-HPLC-UV	Water	20 μL 4 mol/L HCl aqueous solution	-	30	90.1-101.4	0.5-1.0[b]	18
This method	Honey	70μL 1-undecanol	-	1	74.84–112.74	0.95-1.39[a]	

[a] The unit of LOD is μg/kg

[b] The unit of LOD is μg/L

3.1.7 Effect of centrifugation rate

To study the effect of centrifugation rate on the extraction efficiency, the centrifugation rate was varied in the range from 500 to 6500 rpm. As shown in Fig. 7, with the increasement of centrifugation rate from 500 to 3500 rpm, the extraction recoveries increase correspondingly. Because if the centrifugation rate is too low, the separation will not be completed and decrease the recoveries. When the rate exceeded 3500 rpm, the increase of the recoveries remains constantly. Hence, 3500 rpm was chosen as the centrifugation rate in the proposed method.

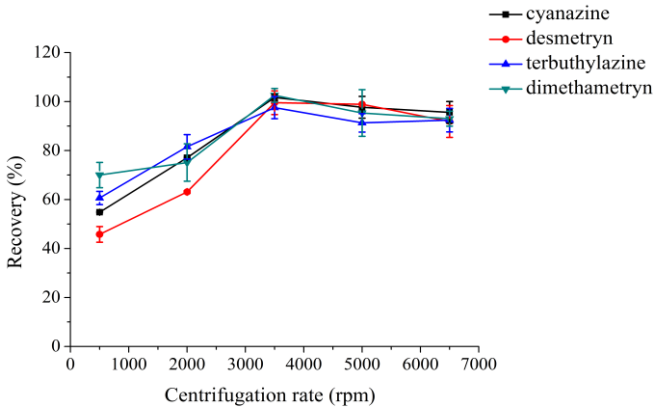

Fig. 7 The effect of centrifugation rate on the extraction recovery of triazines. Experimental condition: the extraction solvent, 1-dodecanol, 70 μL; microwave power, 300 W; microwave irradiation time, 40 s; pH of the sample solution, 5; NaCl concentration, 0%; spiked sample 1 (locust honey) at 90 μg/kg.

3.2 Method validation

3.2.1 Linearity

The working curves were constructed by plotting the corresponding peak areas measured versus the concentrations of triazine herbicides in a series of spiked samples. As listed in Table 1, satisfactory linearity in the concentration range of 5.00-250.00 μg/kg with good correlation coefficients higher than 0.9994 was obtained.

3.2.2. Limit of detection and quantification

The limit of detection (LOD) and limit of quantification (LOQ) were estimated as triazine concentration producing a signal/noise ratio of 3 and 10, respectively. The results obtained are given in Table 1. The LODs and LOQs are in the range of 0.95-1.39 μg/kg and 3.15-4.63 μg/kg, respectively.

3.2.3 Precision and accuracy

The intra- and inter-day precision of the present method were obtained by analyzing the spiked sample at concentrations of 90μg/kg. The intra-day precision was performed by analyzing spiked samples five times in one day. The inter-day precision was analyzed over five days by analyzing spiked samples. As Table 1 shown, acceptable RSD values, ranging from 5.22 to 6.60% and from 3.93 to 6.17% for intra- and inter-day, were obtained respectively. The recoveries in the range of 88.23-100.71% and 85.29-96.45% for intra- and inter-day, were also obtained, respectively.

3.2.4 Application of the method

To demonstrate the practical applicability of the present method, four kinds of spiked honey samples were evaluated by the present method. The typical chromatograms of the blank and spiked sample are shown in Fig. 8, and the analytical results are listed in Table 2. The results indicate that the present method provides good recoveries (74.84-112.74%) and acceptable precision (1.50-13.10%).

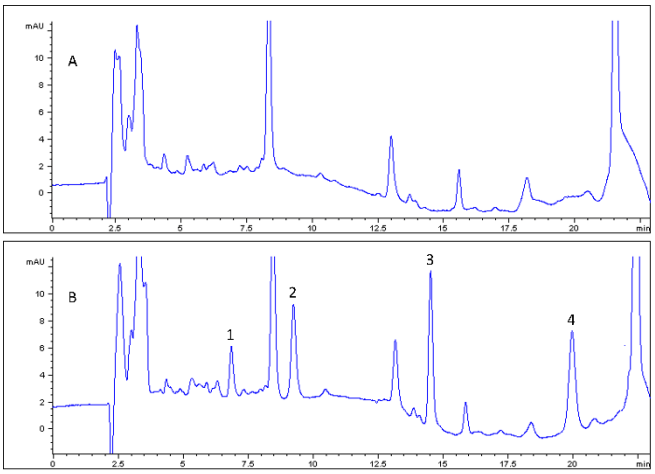

Fig. 8 Typical chromatograms of the blank (A) and spiked sample 1 (locust honey) at 90 μg/kg (B).

3.2.5 Comparison of MA-LLME-SFO with other methods

A comparison of the proposed method with other analytical methodologies reported in the literature was summarized and shown in Table 3. In respects of extraction time, and amount of organic solvent, the proposed method showed superiority over others.

Conclusions

In the present work, as a simple, quick and dispersive-solvent-free method, MA-LLME-SFO was successfully applied for the extraction and analysis of triazine herbicides from honey samples. The method provided satisfactory linearity, repeatability and detection limit. Besides, the whole experiment procedure could be completed within a short time. Moreover, contrast to traditional toxic extraction solvent, such as chlorobenzenze and chloroform, we chose environmentally friendly 1-Dodecanol as a substitute in this method. And the absence of the organic dispersive solvent makes the method more eco-friendly. Therefore, the proposed MA-LLME-SFO method will surely accelerate the development in the analysis of environment pollutants in many complicated matrices.

Acknowledgements

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