Application of an in-situ formulated magnetic deep eutectic solvent for the determination of triazine herbicides in rice

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ABSTRACT

In this work, a rapid, convenient, sensitive, and cost-effective in-situ formed magnetic deep eutectic solvent based on a dispersive liquid-liquid extraction method was developed for the determination of triazine herbicides in rice. A novel tetrabutylammonium chloride (TBAC) based magnetic deep eutectic solvent (MDES), [TBAC/ethylene glycol][FeCl$_4$] was generated by means of a simple in-situ reaction of the deep eutectic solvent (DES) with iron chloride in the sample solution. The solvent which has high affinity for target analytes and magnetic ability was successfully employed as an extraction solvent and simplified both the extraction and separation procedure. A series of parameters influencing the extraction efficiency were investigated. Under optimal conditions, calibration curves for the target triazine herbicides were obtained in the ranges of 5–1000 ng g^{-1}, with correlation coefficients greater than 0.9910. The limits of detection (LOD) and quantification (LOQ) were in the range of 1.49–3.10 ng g^{-1} and 4.96–10.34 ng g^{-1}, respectively. The precision of intra- and inter-day were under 6.2% and 9.6%, respectively, and the precision between laboratories were lower than 7.5%. The accuracy of the method varied from 84.9 to 117.5%. Furthermore, the method showed satisfactory matrix effect and robustness. These results indicate that the technique is suitable for rice sample analysis.

1. Introduction

Generally, triazine herbicides cover a broad-spectrum of applications because of their significant benefits to increasing crop yields [1]. However, it has been shown that the herbicide residues can be accumulated in the human body, resulting in serious problems including cancers, birth defects, and hormone imbalances [2]. To lessen the harmful effect and preserve human health, the European Union (EU) regulates the maximum residue limits (MRLs) of the pesticides in a variety of samples. For rice samples the concentration of triazine herbicides cannot be higher than 0.05 mg kg^{-1} [3]. Consequently, in order to achieve the correct detection for the low concentration of the analytes in the sample, an efficient and reliable pretreatment technique is required.

Dispersive liquid-liquid microextraction (DLLME) method proposed by Rezaee and coworkers [4] can obtain high extraction efficiency by means of forming tiny droplets and increase the contact area between the extractant and sample solution. It has attracted much attention as a promising extraction technique, due to its minimal use of toxic organic solvent, speed, simplicity and compatibility with the environment [5].

DLLME has successfully overcome the drawbacks of classic LLE (liquid-liquid extraction) methods which uses large amounts of organic solvent and is time-consuming [6], therefore resulting in it being widely utilized for the extraction of target analytes [7–9].

Ionic liquids (ILs) are defined as salts composed of organic cations, and either inorganic or organic anions. Due to the superior properties of ILs, including low melting temperature, low vapor pressure, high thermal stability and wide liquid range, they are widely used as alternative solvents in a wide variety of analytical fields [10,11]. However, in practice, ILs have complex synthetic processes, a high price and potential toxicity, restricting their further application [12]. In recent years, deep eutectic solvents (DESs) which can be easily prepared by means of mixing hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA) have attracted tremendous attention [13–15]. They have similar abilities to ILs, and furthermore, they have less toxicity, cheaper and simpler synthetic process [16,17]. Therefore, as substitutes for ILs, they have been successfully applied broadly in a variety of fields such as gas absorption, drug dissolution, electrodeposition of metals, analysis of target analytes from products, and the synthesis of nanoparticles

[18–22].

MILs (magnetic ionic liquids) are a special subclass of ILs, exhibiting susceptibility to external magnetic fields [23]. Thus, MILs can be fast and conveniently isolated via magnetic separation in sample pretreatment. Based on this superior property, in the previous study, Hayashi et al. were firstly introduced MILs [bmim][FeCl$_4$] and Wang et al. utilized [C$_6$mim] [FeCl$_4$] as an extraction solvent for triazine herbicides [25,26]. Similar to MILs, magnetic deep eutectic solvents (MDES), [choline chloride/phenol][FeCl$_4$] was proposed to be used in sample pretreatment [27].

In this work, in-situ formed magnetic deep eutectic solvent based on a dispersive liquid-liquid extraction method for the determination of triazine herbicides in rice samples is proposed. Herein, a novel magnetic DES [tetrabutylammonium chloride][ethylene glycol][FeCl$_4$] has high affinity for triazine herbicides and greatly simplifies the extraction procedure through magnetic separation and collection was in-situ generated by simple agitation of DES with a magnetized agent iron chloride. According to our knowledge, this demonstrates the first introduction of both TBAC based DES as a magnetic DES, and the in-situ formation of DES in a sample solution. To achieve optimal extraction conditions, a variety of experimental parameters were investigated. Under optimal conditions, method validation was processed in terms of evaluating linearity, limit of detection (LOD) and quantification (LOQ), precision, accuracy, matrix effect and robustness.

2. Materials and methods

2.1. Reagents

Five standard triazine herbicides, desmetryn, secbumeton, terbumeton, terbuthylazine and prometryn were all purchased from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Standard stock solutions of the triazine herbicides were prepared in chromatographical acetonitrile at a concentration of 500 μg/mL.

Mixed working solution (20 μg/mL) was prepared by diluting and mixing single standard solution. These solutions were stored at 4 °C.

Chromatographical acetonitrile was purchased from Fisher Scientific Company (UK). Tetrabutylammonium chloride (>99%) was obtained from Chengjie Chemical Co. LTD. (Shanghai, China). Ethylene glycol was purchased from Aladdin Bio-chem Technology Co., LTD. (Shanghai, China). Carbonyl iron powder (CIP) was purchased from Jilin Jien Nickel Industry (Panshi, China). Other reagents including n-hexane, iron chloride and diethyl ether were of analytical grade and were purchased from Beijing Chemical Factory (Beijing, China).

2.2. Instruments

HPLC analysis was carried out using LC-20ADXR liquid chromatograph (Shimadzu, Japan), equipped with two LC-20AD pumps, an SIL-20A automated sample injector, a CTO-20A column oven and an SPD-20A UV–Vis detector. An eclipse XDB-C18 column (150 mm × 4.6 mm, with 3.5 μm particle size; Agilent Technologies Inc., USA) was employed for separation. SZCL-2 magnetic stirrer was purchased from Yuhua Instrument Co., Ltd. (Gongyi, China) and Vortex-5 vortex shaker was purchased from Kylin-Bell Lab Instruments Co., Ltd. (Haimen, China).

HPLC conditions were optimized in the laboratory and the HPLC analysis was conducted with gradient program, acetonitrile (A) and water (B) were used as mobile phase. The gradient condition was as follows: 0–5 min, 75-70% B; 5–10 min, 70% B; 10–15 min, 70-65% B; 15–25 min, 65% B; 25–30 min, 65-60% B; 30–40 min, 60% B. The flow rate was set at a constant flow of 0.8 mL/min, and the detection wavelength was 220 nm. The sample injection volume was 20 μL.

2.3. Sample preparation

Two kinds of rice samples (sample 1, sample 2) and a maize sample (sample 3) were collected from a local supermarket. They were powdered with a crusher and added appropriate amount of mixed standard solutions of triazine herbicides, then, mixed with them to prepare spiked samples and they were preserved in 4 °C. Except for section 3.3, all experiments were proposed using sample 1.

2.4. Preparation of DESs

DESs were prepared by mixing ethylene glycol and tetrabutylammonium chloride at four different molar ratio (1:1, 2:1, 3:1, 4:1) and heated at temperature of 80 °C for 30 min under constant stirring. After processing, stable homogeneous liquids were obtained. The prepared DESs were stored in sealed laboratory vials and kept in a desiccator.

2.5. In-situ formed magnetic DES based on DLLME extraction procedure

An aliquot of 1 g spiked rice sample (150 ng g^{-1}) was weighed and ultrasonicated in 4 mL x-hexane for 5 min, and centrifuged at 6000 rpm for 5 min, subsequently, the supernatant was then separated for further analysis. Then, 250 μL of DES (molar ratio of ethylene glycol to TBAC was 2:1) was added to the sample solution and vortexed for 4 min to enrich the analytes to the DES phase. After adsorption, 40 mg of iron chloride was carefully weighed and added into the solution to in-situ form the magnetic DES. After shaking to homogenize for 5 min and form the magnetic DES, 90 mg of CIP was added to enhance the magnetic properties and the DES phase was collected with an external magnet. Following the dissolution of target analytes in 5 mL of diethyl ether, the diethyl ether phase was separated and dried under a nitrogen gas stream. An aliquot of 100 μL chromatographical acetonitrile was added to re-dissolve the target analytes and 20 μL was injected into the HPLC system for analysis. The chemistry of DES formation is displayed in Fig. 1 and the in-situ formed magnetic DES based on DLLME extraction procedure is shown graphically in Fig. 2.

3. Results and discussion

3.1. Optimization of the method

To quantify the effect of the parameters on the extraction efficiency, volume of DES, molar ratio of HBD and HBA, amount of iron chloride, amount of carbonyl iron powder, extraction time and elution solvent volume were carried out to be optimized. All the experiments were performed in triplicate at the concentration of 150 ng g^{-1}.

3.1.1. Effect of DES volume

Regarding the DES is the only extractant for extracting target analytes, volume of DES has an important role in the extraction procedure. The extraction performance was evaluated by varying the volume of DES from 100 to 300 μL. As depicted in Fig. 3, when the volume increased from 100 to 250 μL, the recoveries of the five triazine herbicides were enhanced, however, when more than 250 μL of DES used, the recoveries didn't have significant changes. It indicates that 250 μL DES was sufficient to extract target analytes. Therefore, 250 μL of DES was utilized for the subsequent process.

3.1.2. Effect of HBD and HBA molar ratio

The selection of a suitable molar ratio for HBD and HBA is crucial to obtain the greatest extraction efficiency. In this work, ethylene glycol and TBAC were employed as the HBD and HBA respectively. For the purpose of this work, four kinds of DES with differing ratios were investigated. As exhibited in Fig. 4, the best extraction efficiency was achieved with ratio 2. It can be attributed that when the molar ratio was 1:1, a sticky paste of DES which cannot be completely dispersed in
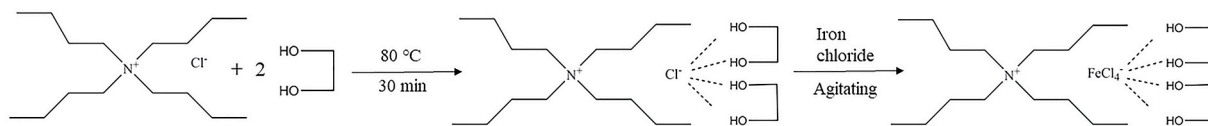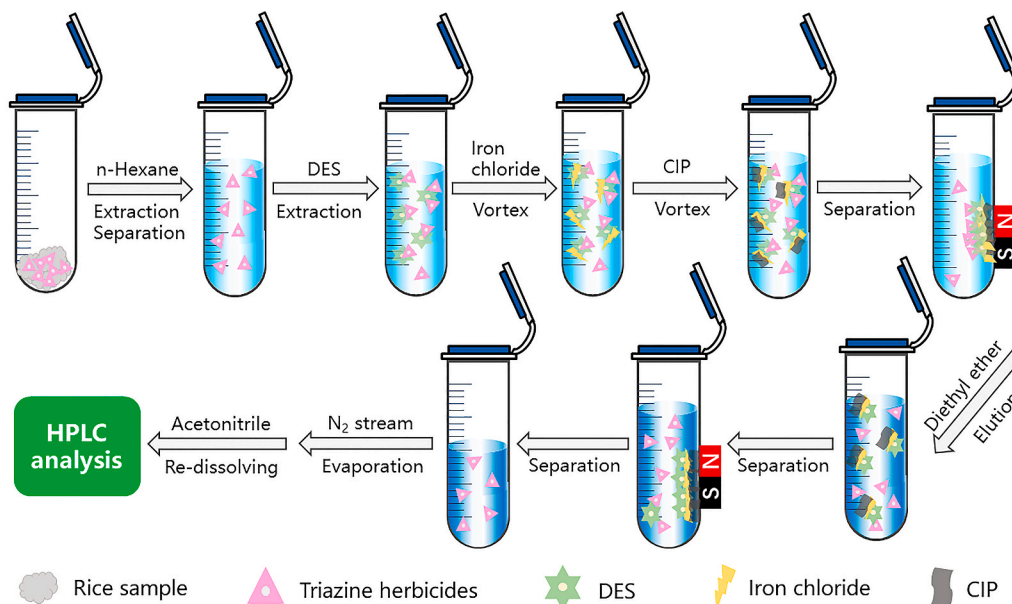
Fig. 1. Interaction of the MDES components.

Fig. 2. In-situ formed MDES based on DLLME extraction procedure.
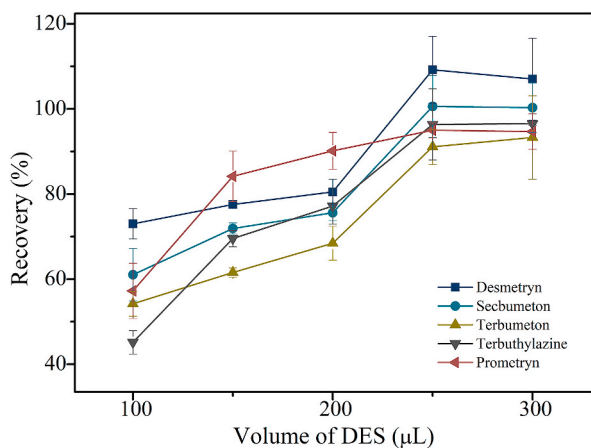

Fig. 3. Effect of DES volume on recovery. Molar ratio of HBD to HBA, 2:1; amount of iron chloride, 40 mg; carbonyl iron powder amount, 90 mg; extraction time 4 min; volume of elution solvent, 5 mL.
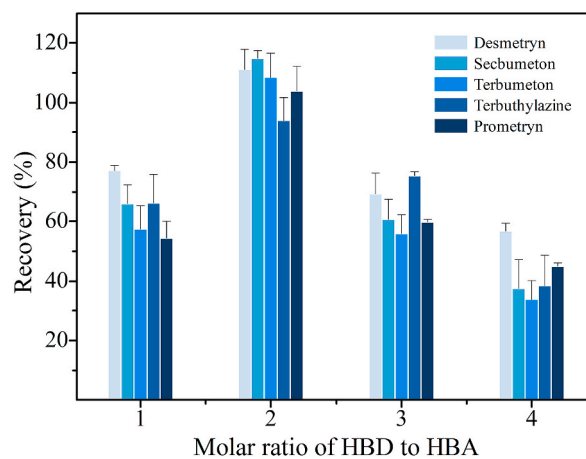

Fig. 4. Effect of molar ratio of HBD to HBA on recovery. DES volume, 250 μL; amount of iron chloride, 40 mg; carbonyl iron powder amount, 90 mg; extraction time 4 min; volume of elution solvent, 5 mL.

sample solution was formed, moreover, a component of DES, TBAC has higher affinity for target analytes than that of ethylene glycol, as a result, greatest extraction efficiency was obtained when the molar ratio was 2:1. Thus, the optimal ratio of HBD to HBA was selected to be 2:1.

3.1.3. Effect of amount of iron chloride

In order to effectively magnetize the DES, a sufficient amount of iron chloride was necessary. The effect of iron chloride amount on the extraction recovery of it was investigated and the amount was varied from 10 to 50 mg. As shown in Fig. 5, the increasing iron chloride mass led to the enhancement of recovery until the amount was 40 mg. Whereas, no significant increase was performed over 40 mg. Therefore,

40 mg of iron chloride was employed to magnetize the DES in the subsequent process.

3.1.4. Effect of carbonyl iron powder amount

Carbonyl iron powder (CIP) can be magnetically attracted by the MDES in the sample solution. Therefore, it was used to enhance the magnetic ability of MDES and shorten the magnetic separation time. The effect of CIP amount was investigated by increasing the amount from 60 to 100 mg. As shown in Fig. 6, 90 mg of CIP was sufficient to attract the MDES. Therefore, 90 mg was selected in the subsequent process.
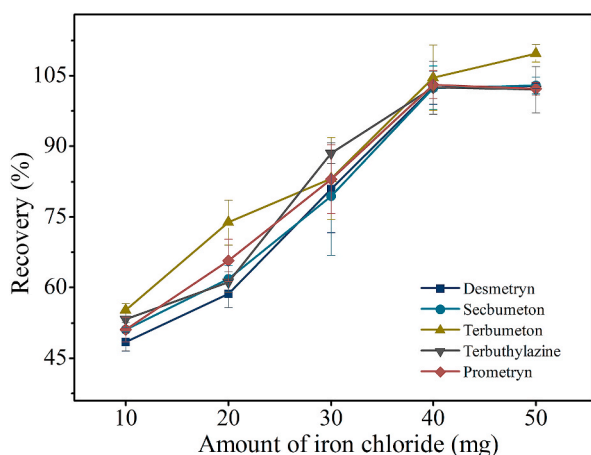
Fig. 5. Effect of amount of iron chloride on recovery. DES volume, 250 µL; molar ratio of HBD to HBA, 2:1; carbonyl iron powder amount, 90 mg; extraction time 4 min; volume of elution solvent, 5 mL.
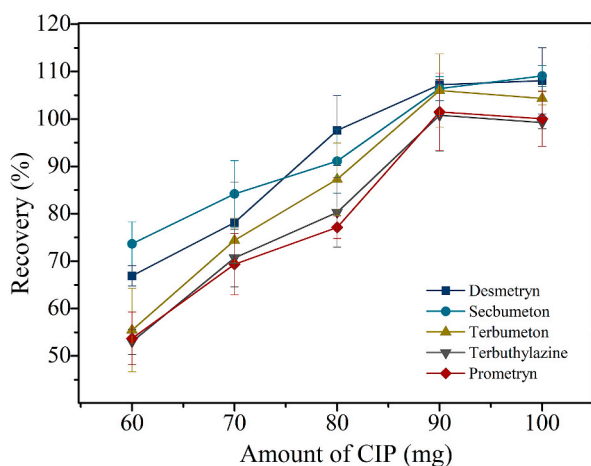

Fig. 6. Effect of carbonyl iron powder amount on recovery. DES volume, 250 µL; molar ratio of HBD to HBA, 2:1; amount of iron chloride, 40 mg; extraction time 4 min; volume of elution solvent, 5 mL.
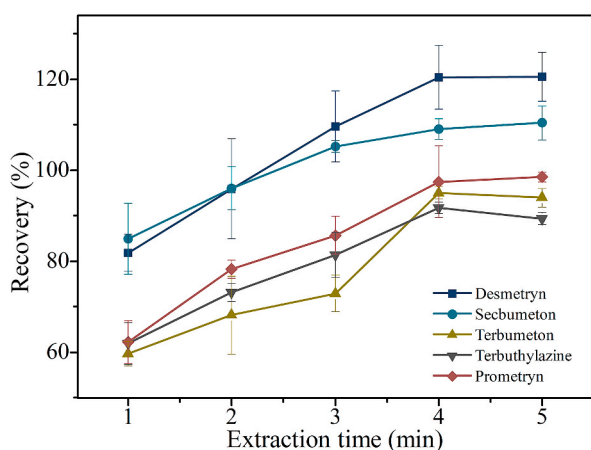
3.1.5. Effect of extraction time

The effect of extraction time was evaluated by increasing the time from 1 to 5 min. As seen in Fig. 7, the recoveries were increased with the enhancement of extraction time from 1 to 4 min and remained stable with a further time increase. Hence, 4 min was selected in the subsequent process.

3.1.6. Effect of elution solvent volume

Many elution solvents, such as methanol or acetonitrile are not feasible for elution of target analytes due to a high affinity for DES, whose wide chromatographic peaks can wrongly influence the correct measurement of target analytes. Diethyl ether with high affinity for triazine herbicides can overcome this problem due to the low affinity for DES. Based on these considerations, diethyl ether was considered as an appropriate elution solvent. The effect of varying the amount of elution solvent from 2 to 6 mL of diethyl ether was investigated, and the results are displayed in Fig. 8. It can be seen in that 5 mL was sufficient to elute the target analytes. Therefore, 5 mL diethyl ether was selected in the subsequent process.

3.2. Method validation

To evaluate the performance of the proposed method, linear ranges, correlation coefficients (r), LODs, LOQs, reproducibility, recovery of the triazine herbicides, matrix effect and robustness were calculated.

The linearity of the method was measured by means of plotting the corresponding peak area of each triazine herbicide at the seven concentrations. As seen in Table 1, the obtained linearities of five target analytes were within 5–1000 ng g^{-1} and 10–1000 ng g^{-1} with satisfactory correlation coefficient (r) greater than 0.9910.

LODs and LOQs which were determined based upon a signal-to-noise ratio of 3 and 10 were 1.49–3.10 ng g^{-1} and 4.96–10.34 ng g^{-1} respectively. The LODs were lower than the MRLs (0.05 µg g^{-1}) of triazine herbicides in the rice samples.

Precision of the method was evaluated in terms of the intra-day, inter-day and reproducibility. As depicted in Table 2, intra-day RSDs measured five times a day and inter-day RSDs calculated over five consecutive days were lower than 6.2% and 9.6%, respectively. Furthermore, precisions between four different laboratories were lower than 7.5%. The corresponding recoveries were varied from 84.9 to 117.5%.

Matrix effect which is used to evaluate the influence of co-extracted compounds from sample solution to the determination of target analyte was calculated. The obtained matrix effects of five triazine herbicides were 3.5%, 4.1%, −2.5%, 5.2% and −3.1% respectively. The results can

Fig. 7. Effect of extraction time on recovery. DES volume, 250 µL; molar ratio of HBD to HBA, 2:1; amount of iron chloride, 40 mg; carbonyl iron powder amount, 90 mg; volume of elution solvent, 5 mL.

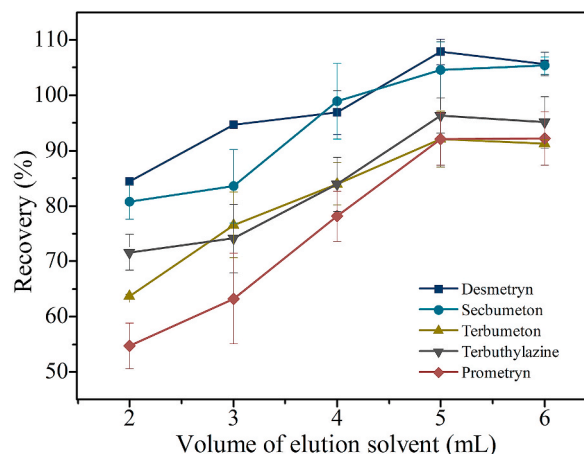**Fig. 8.** Effect of volume elution solvent on recovery. DES volume, 250 µL; molar ratio of HBD to HBA, 2:1; amount of iron chloride, 40 mg; carbonyl iron powder amount, 90 mg; extraction time 4 min.

Table 1
Analytical performances of the present method.

Analyte	Liner range (ng/g)	Regression equation	Correlation coefficient (r)	LOD (ng/g)	LOQ (ng/g)
Desmetryn	10–1000	A = 903.8b + 278	0.9916	3.10	10.34
Secbumeton	5–1000	A = 2077.2b + 259	0.9934	1.49	4.96
Terbumeton	10–1000	A = 1673.2b + 226	0.9981	2.12	7.06
Terbuthylazine	5–1000	A = 2085.9b + 424	0.9910	1.63	5.45
Prometryn	10–1000	A = 1324.1b + 252	0.9933	2.61	8.71

demonstrate that the matrix effects were acceptable.

Robustness was introduced to evaluate the stability of the performance of the method when the experiment parameters were slightly changed. Robustness was evaluated using the "seven parameters/eight experiments" design proposed by Youden robustness test. In the experiment, volume of DES, hexane and diethyl ether, amount of iron chloride and CIP, % of acetonitrile in the mobile phase and flow rate were chosen as seven parameters. The eight experiments and related calculated results were shown in Tables S1–S3. The obtained robustness were 3.9, 2.7, 2.8, 2.2 and 2.8 respectively, which were all lower than precision of the method. It can sufficiently demonstrate that the slight changes of the parameters were not able to significantly influence the performance of the method and also, can show that the proposed method had satisfactory robustness.

3.3. Analysis of real samples

In order to evaluate its accuracy and reliability, the method was tested on a maize sample, which is also common product in our daily life and may contain triazine herbicide residues (established MRLs in the maize are $0.05 \, \text{mg kg}^{-1}$) and two kinds of rice samples at concentrations of 30, 150, and $300 \, \text{ng g}^{-1}$ using the external standard method. As summarized in Table 3, the recoveries were in the range of
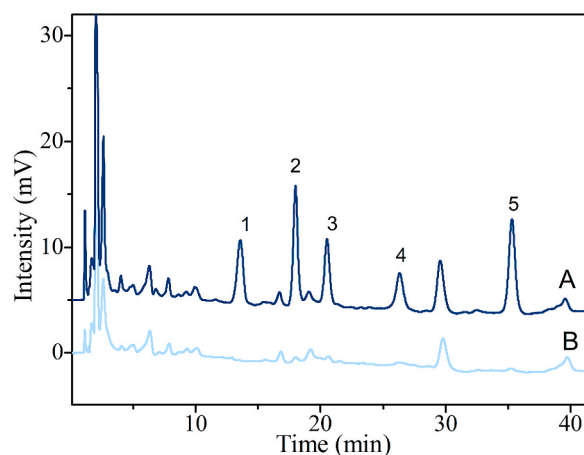
Fig. 9. HPLC chromatograms of blank rice sample 1 (A) and spiked sample 1 (B). Peaks: 1, desmetryn; 2, secbumeton; 3, terbumeton; 4, terbuthylazine; 5, prometryn. Spiked concentration, $150 \, \text{ng g}^{-1}$.

Table 2
Intra- and inter-day precisions and precision between laboratories of the present method.

Precision	Analytes	Desmetryn		Secbumeton		Terbumeton		Terbuthylazine		Prometryn	
	Spiked (ng/g)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Intra-day precision (n = 5)	30	92.5	4.1	99.3	2.1	100.1	3.9	99.8	4.4	94/3	3.4
	150	117.5	4.9	108.4	2.7	92.3	1.8	88.1	1.9	93.7	6.2
	300	99.5	4.6	106.1	5.9	105.1	3.0	101.4	1.9	108.3	4.8
Inter-day precision (n = 5)	30	94.6	8.0	95.2	3.7	89.6	5.3	99.2	2.5	88.5	4.9
	150	107.1	6.2	102.2	7.0	94.8	9.6	93.7	6.2	92.9	2.6
	300	97.1	7.6	100.5	2.0	111.5	4.5	101.3	3.2	98.8	6.8
Precision between laboratories (n = 4)	30	92.5	5.7	101.9	7.1	96.4	2.0	101.4	6.2	84.9	4.4
	150	107.9	7.1	108.4	5.6	100.3	7.3	108.5	5.4	91.3	7.5
	300	103.4	3.5	105.5	6.9	105.2	1.8	102.6	3.7	96.4	6.4

Table 3
Analytical results of real samples.

Matrix	Spiked (ng/g)	Desmetryn		Secbumeton		Terbumeton		Terbuthylazine		Prometryn	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Rice 1	30	84.0	6.2	82.3	5.1	83.8	5.9	106.8	1.1	77.9	6.0
	150	116.5	6.3	117.2	4.9	113.1	3.6	108.6	1.9	116.7	8.9
	300	114.4	6.8	115.6	6.5	107.1	8.0	116.1	8.1	114.2	8.9
Rice 2	30	105.3	4.9	91.5	6.8	87.1	6.1	86.4	4.9	109.8	1.9
	150	110.9	7.8	84.8	3.7	83.0	2.5	96.4	4.7	99.5	7.5
	300	109.3	6.1	90.0	2.4	80.1	5.2	105.9	4.1	108.6	8.1
Maize	30	86.7	3.9	83.1	7.7	91.9	5.9	95.5	3.4	100.2	9.1
	150	105.1	2.9	78.2	2.8	81.7	1.5	94.3	2.9	89.3	7.3
	300	97.0	7.3	84.0	7.9	78.5	9.1	89.1	8.6	93.6	7.4

Table 4

Comparison of the present method with previously reported methods.

Matrix	Analyte	Extraction method	Extraction agent	Analytical instrument	Linear range (ng g^{-1})	LOD (ng g^{-1})	Recovery (%)	Refs.
Oilseed	Triazine herbicides	MSPD-DLLME	Magnetic ionic liquid	UFLC-UV	8–1000	1.20–2.72	86–106	[28]
Corn	Atrazine	MISPE	Methacrylic acid	LC-MS	10–100	1.6–3.3	80.2–119.1	[29]
Honey	Triazine herbicides	DLLME	Ionic liquid	HPLC-UV	29.4–912	5.31–8.59	60.1–133	[30]
Rice	Polar acidic herbicides	MSPE	Fe_3O_4@PEI-RGO	HPLC-UV	2–300	0.67–2.0	87.4–102.5	[31]
Peanut	Triazine herbicides	LSE-dSPE	MOF-101 (Cr)	HPLC-UV	3.1–200	0.98–1.90	89.5–102.7	[32]
Cereal	Triazine herbicides	DMAE	Methanol/1-dodecanol	HPLC-UV	10–500	1.1–1.5	80.0–102.0	[33]
Rice	Triazine herbicides	DLLME	Magnetic deep eutectic solvent	HPLC-UV	5–1000	1.49–3.10	84.9–117.5	This work

77.9–117.2%, with RSDs lower than 9.1%. In addition, both of blank (non-spiked) and spiked rice samples were analyzed, and the corresponding chromatograms were shown in Fig. 9, indicate that none of the analytes were detected in the real rice sample.

3.4. Comparison with other method

The present method was compared with other previously reported studies [28–33]. As seen in Table 4, the method provided similar or lower LODs when compared to these studies. The method is also simpler, cheaper and requiring both less extraction time and organic solvent. As a result, the method can be evaluated as a compatible and reliable technology.

4. Conclusion

In the present study, a rapid, sensitive, easy and eco-friendly extraction method, using an in-situ formed magnetic DES based DLLME method, for the determination of triazine herbicides in rice sample was proposed. Herein, a new magnetic TBAC based DES, as well as in-situ magnetization technology for formulating the MDES has been proposed, it largely simplified both the extraction and separation procedure. Under the optimal conditions, satisfactory linearity, precision, accuracy, matrix effect and robustness were obtained. In conclusion, the present method has great potential for analyzing triazine herbicides in rice samples.

Credit author statement

The specific work of each author in this study was as follows: Huilan Piao: participated and design in the whole work; drafting of this article; data analysis. Yanxiao Jiang: participation in part of the work. Zucheng Qin: participation in part of the work. Pinyi Ma: guidance in the revision of experimental manuscripts. Ying Sun: guidance in the revision of experimental manuscripts. Xinghan Wang: guidance in the revision of experimental manuscripts. Daqian Song: guidance in the revision of experimental manuscripts. Qiang Xei: guidance and final approval of the version to be published.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2020.121527.

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