Food Chemistry: X 18 (2023) 100711

Contents lists available at ScienceDirect

Food Chemistry: X

journal homepage: www.sciencedirect.com/journal/food-chemistry-x

Analytical Methods

Magnetic deep eutectic solvent-based dispersive liquid–liquid microextraction for determination of strobilurin fungicides in water, juice, and vinegar by high-performance liquid chromatography

Min Wang [a,b], Luyao Zhao [a], Yu Niu [c], Shu Qin [d], Lixin Zhang [a,*], Liyan Jia [a,b,*], Xu Jing [a,b,*]

[a] College of Food Science and Engineering, Shanxi Agricultural University, Taigu, Shanxi 030801, China
[b] Graduate Education Innovation Center on Baijiu Bioengineering in Shanxi Province, Taigu, Shanxi 030801, China
[c] Agricultural Economics and Management College, Shanxi Agricultural University, Taiyuan, Shanxi 030006, China
[d] Shanxi Center for Testing of Functional Agro-Products, Shanxi Agricultural University, Taiyuan, Shanxi 030031, China

ARTICLE INFO

Keywords:
Hydrophobic deep eutectic solvents
Magnetic deep eutectic solvents
Strobilurin fungicides
Dispersive liquid–liquid microextraction
High-performance liquid chromatography

ABSTRACT

In this study, a magnetic deep eutectic solvent coupled with dispersive liquid–liquid microextraction using high-performance liquid chromatography (MDES-DLLME-HPLC) was developed to detect strobilurin fungicides. The green hydrophobic MDES synthesized by methyltrioctylammonium chloride, ferric chloride, and heptanoic acid was used as an extraction solvent, which was dispersed by vortex and separated by an external magnetic field. The use of toxic solvents was avoided, and the separation time was reduced. The best experimental results were obtained through single factor and response surface optimization. The method had a good linear relationship with $R^2 > 0.996$. The limit of detection (LOD) ranged from 0.001 to 0.002 mg L^{-1}. The extraction recoveries were 81.9–108.9%. The proposed method was rapid and green, and it has been successfully applied to detection of strobilurin fungicides in water, juice, and vinegar.

1. Introduction

Strobilurin fungicides are the largest-selling fungicides (Jing, Huang, Zhang, Wang, Xue, Wang, et al., 2022), mainly including azoxystrobin, pyraclostrobin, trifloxystrobin, *etc.* (Zhang, Zhou, Xu, Du, Li, Wang, et al., 2020). They are extensively applied in fruits, cereals, and vegetables (Jia, Huang, Zhao, Wang, & Jing, 2020). Strobilurin fungicides improve agricultural crop yields, but their residues may pose a threat to human health (Kovacevic, Hackenberger, & Hackenberger, 2021; Song, Li, Yan, Tian, Ren, Jiang, et al., 2022). The maximum residue limits of strobilurin fungicides in food products have arisen wide concern (Liu, Hu, Feng, Liu, Xie, Chai, et al., 2022). The establishment of a rapid and green detection method of strobilurin fungicide residues can better ensure food safety.

Dispersive liquid–liquid microextraction (DLLME) was developed to separate and enrich analytes (Rezaee, Assadi, Milani Hosseini, Aghaee, Ahmadi, & Berijani, 2006). The dispersion and extraction solvents were mixed and quickly injected into an aqueous solution; the analytes were then extracted into dispersed tiny droplets (Monajemzadeh, Mohebbi, Farajzadeh, Nemati, & Mogaddam, 2021; Nemati, Farajzadeh, Mogaddam, Mohebbi, Azimi, Fattahi, et al., 2022). This extraction method has been widely applied due to its rapidity, simple operation, high recovery, and low cost (Farajzadeh, Kiavar, & Pezhhanfar, 2021; Zhao, An, Sun, He, Jiang, & Zhang, 2021). However, there are some disadvantages, (i) harmful dispersants and extraction solvents are still used (Hussin, Varanusupakul, Kassim, Rozi, & Mohamad, 2021; Sadeghi, Tehrani, & Faraji, 2022); (ii) a time-consuming centrifugation process is still required for the phase separation (Qiao, Tao, Yao, Zhao, & Yan, 2022).

To address the first disadvantage, vortex, ultrasonication, microwave irradiation, and other methods were adopted to exclude the use of toxic dispersants in recent years. A vortex is an effective and low-cost dispersion method (Psillakis, 2019). The extraction solvent was dispersed as fine droplets with the help of a vortex agitator, which greatly increased the interfacial area and the extraction efficiency so that analytes could reach the distribution equilibrium in a few minutes (Lemos, Barreto, Santos, de Assis, Novaes, & Cassella, 2022).

As another approach to address the first disadvantage, deep eutectic solvents (DESs) with green properties are gradually emerging to overcome the disadvantage of using toxic extraction solvents. DESs have

* Corresponding authors at: College of Food Science and Engineering, Shanxi Agricultural University, Shanxi 030801, China.
E-mail addresses: 13934600160@139.com (L. Zhang), liyangjia1979@163.com (L. Jia), x.jing@vip.163.com (X. Jing).

https://doi.org/10.1016/j.fochx.2023.100711
Received 25 November 2022; Received in revised form 4 May 2023; Accepted 7 May 2023
Available online 10 May 2023

favorable properties such as sustainability, biodegradability, accessibility, and good thermal stability (El Achkar, Greige-Gerges, & Fourmentin, 2021; Nian & Li, 2022). In addition, its preparation is simple, fast, with no by-products, and purification requirements (Zhang, Li, Yao, Yi, Shen, Li, et al., 2022). DESs are regarded as excellent alternatives to conventional organic solvents for safe, green extraction.

To address the second disadvantage, magnetic solvents have gradually been introduced to reduce the time required for phase separation in recent years. They can be easily separated and collected without tedious, time-consuming centrifugation steps, enabling fast sample pretreatment (Farooq, Tryon-Tasson, Biswas, & Anderson, 2022; Omar & Sadeghi, 2022). Compared with magnetic materials, magnetic solvents show simpler preparation and better repeatability. Magnetic ionic liquids not only have a low vapor pressure and high thermal stability but also can respond strongly to external magnetic fields (Ghasemi, Mirzaei, Mogaddam, Khandaghi, & Javadi, 2022), but they are expensive and require drying or a rotary evaporation process (Yao & Du, 2020). Magnetic deep eutectic solvents (MDESs) not only have paramagnetic properties similar to magnetic ionic liquids but also demonstrate other significant advantages such as low cost and easy availability (Farooq, Tryon-Tasson, Biswas, & Anderson, 2022). Currently, most of MDESs are hydrophilic, therefore they have a narrow range of applications and can only be used to extract polar analytes (such as thiophene and aldehydes) in non-polar solvents (such as *n*-heptane and oil samples) (Babaee & Daneshfar, 2018; Khezeli & Daneshfar, 2017). Hydrophobic MDESs are rarely reported, which limits the application of MDESs in extracting analytes from food products. At present, most hydrophobic MDESs still utilize the synthesis method of ionic liquids instead of DESs. On the one hand, toxic solvents should be used to assist the synthesis, such as dichloromethane, methanol, and chloroform. On the other hand, the synthesis is time-consuming and requires the usage of a rotary evaporator and vacuum oven (Farooq, Tryon-Tasson, Biswas, & Anderson, 2022; Wang, Liu, Peng, & Ding, 2021). A simple, rapid, and green method is expected to synthesize hydrophobic MDESs in tens of minutes for efficient extraction of pesticide residues from aqueous samples without the use of toxic solvents, rotary evaporator, and vacuum oven.

In this study, a MDES coupled with DLLME using high-performance liquid chromatography (HPLC) was developed to detect strobilurin fungicides. The green hydrophobic MDES [methyltrioctylammonium chloride] [ferric chloride] [heptanoic acid] was designed, synthesized, and coupled with vortex for dispersion microextraction. The separation time was shortened due to the magnetic response. Thus, the proposed method shows the advantages of environmental friendliness and high efficiency. The extraction conditions were optimized by single-factor and response surface methods. This rapid and green extraction method can be used to detect strobilurin fungicides in water, juice, and vinegar by using HPLC.

2. Materials and methods

2.1. Reagents and chemicals

Azoxystrobin, pyraclostrobin, and trifloxystrobin (98%) were obtained from China Agricultural University (Beijing, China). Triethylmethylammonium chloride (TMAC), methyltributylammonium chloride (MeTAC), methyltrioctylammonium chloride (MTAC), ferric chloride, heptanoic acid, octanoic acid, nonanoic acid, and decanoic acid were purchased from Aladdin Co., Ltd (Shanghai, China). Carbonyl iron powder (CIP) was purchased from Macklin Co., Ltd (Shanghai, China). Organic phase needle filter (nylon) was purchased from ANPEL Laboratory Technologies Co., Ltd (Shanghai, China). Water, juice, and vinegar were purchased from local markets (Jinzhong, China).

2.2. Instrumentation

Azoxystrobin, pyraclostrobin, and trifloxystrobin were investigated using Agilent 1260 HPLC with a G1315D diode-array detector (Beijing, China). The chromatographic column was a Dikma Diamonsil C_{18} (250 × 4.6 mm, 5 μm) device. After the pre-experiment, the chromatographic methods were developed. The mobile phase were methanol and water (78:22 v/v). The flow rate and injection volume were 0.5 mL min^{-1} and 20 μL, respectively. The detection wavelengths of azoxystrobin, pyraclostrobin, and trifloxystrobin were 255, 275, and 251 nm, respectively (Fig. S1).

2.3. Preparation of the MDES

Methyltrioctylammonium chloride, ferric chloride, and heptanoic acid in the molar ratio of 0.5:0.08:6 could be mixed in a 10-mL centrifuge tube and then heated at 80 °C for five minutes to form a homogeneous liquid (Jing, Xue, Sang, Wang, & Jia, 2022). The physical properties (Table S1) and characterization of the MDES, such as phase diagram (Fig. S2), infrared spectroscopy (Fig. S3), nuclear magnetic resonance (Fig. S4), and scanning electron microscopy (Fig. S5) were shown in the supplementary material.

2.4. MDES-DLLME step

Some 5 mL of sample solution and 200 μL of the MDES were added into a 10-mL centrifuge tube and vortexed for 3 min. Then 90 mg of CIP was added to assist the collection of the MDES phase under an external magnetic field. Finally, the MDES phase was filtered with a 0.22-μm filter membrane, and 110 ± 5 μL of MDES was collected and detected by HPLC (Fig. 1).

3. Results and discussion

3.1. Response surface optimization of extraction conditions

A Box-Behnken design was applied to determine the optimal molar ratio of the MDES. Other invariable conditions were as follows: the hydrogen-bond acceptor (HBA) was MTAC, the hydrogen-bond donor (HBD) was heptanoic acid, the volume of the MDES was 200 μL, the vortex time was 60 s, and the amount of CIP was 90 mg. The independent variables were the molar ratio of MTAC (A: 0.1–0.9), $FeCl_3$ (B: 0.01–0.15), and heptanoic acid (C: 1–11). The dependent variable was the average extraction recovery (ER) of strobilurin fungicides (Y) (Table S2).

The effect of the molar ratio of the MDES on the average ER of strobilurin fungicides was estimated using Design-Expert® 12 software (Stat-Ease, Inc., Minnesota, America). The fitting equation was as follows: $Y = + 82.47 - 2.48A + 1.44B - 2.12C + 2.74A\,B + 3.26AC - 1.39BC - 9.89A^2 - 3.28B^2 - 5.05C^2$. According to the analysis of variance (ANOVA) (Table S3), the F-value was 19.32, and the P-value was less than 0.05. Therefore, the quadratic model was statistically significant. The lack of fit F-value of 0.32 implies that the lack of fit was not significant relative to the pure error; because R^2 was 0.9613, there was little difference between the adjusted and predicted R^2 values (<0.2). This showed that the model and data were reliable and could be used for response prediction. According to the 3D response surface as shown in Fig. 2, the molar ratio of MTAC (A), $FeCl_3$ (B), and heptanoic acid (C) played an important role in the extraction recovery. According to the experimental results, the optimal molar ratio MTAC: $FeCl_3$: heptanoic acid was 0.5:0.08:6. Under the optimal molar ratio, the theoretical maximum ER was 83.1%. After experimental verification, the ER was 88.5% under optimal conditions.

3.2. Single factor optimization of extraction conditions

The type of MDESs, the volume of MDES, the vortex time, and the amount of CIP were optimized to determine the optimal extraction conditions. Each experiment was repeated three times.

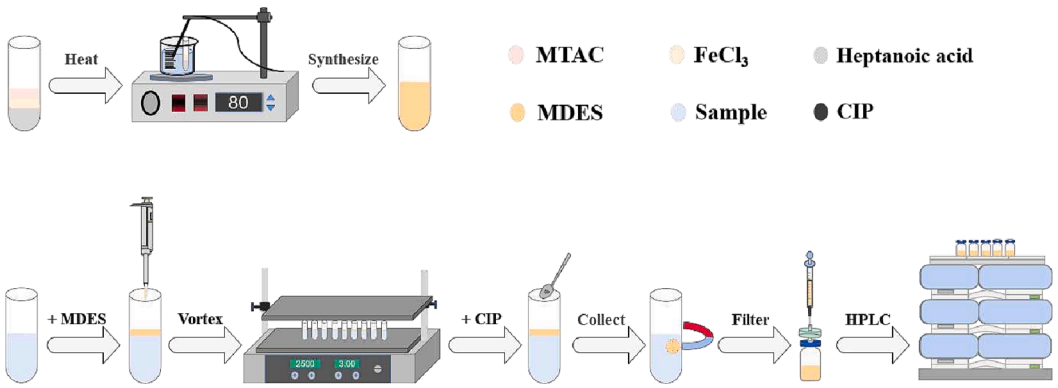

Fig. 1. The flow chart through the MDES-DLLME-HPLC process.

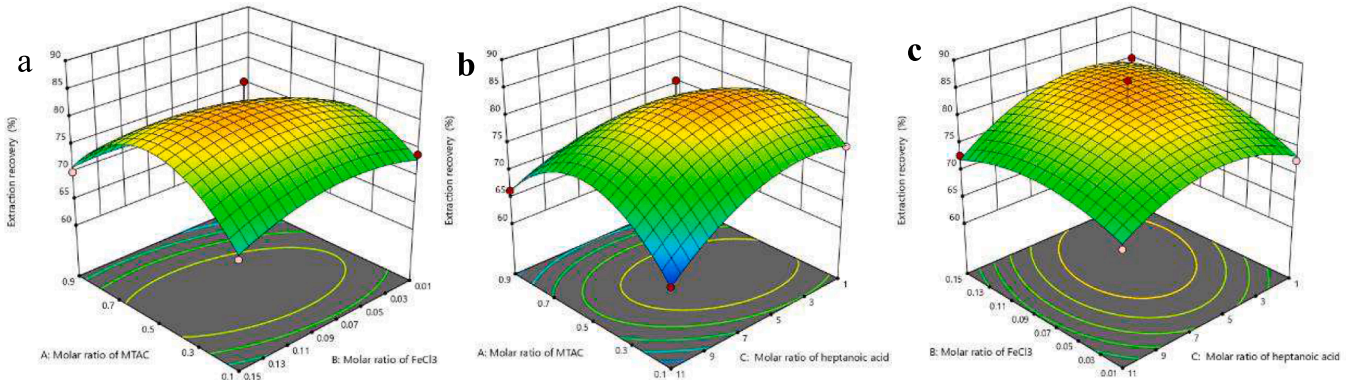

Fig. 2. Response surface optimization of the extraction conditions. (a: the effects of different molar ratios of MTAC and $FeCl_3$. b: the effects of different molar ratios of MTAC and heptanoic acid. c: the effects of different molar ratios of $FeCl_3$ and heptanoic acid.).

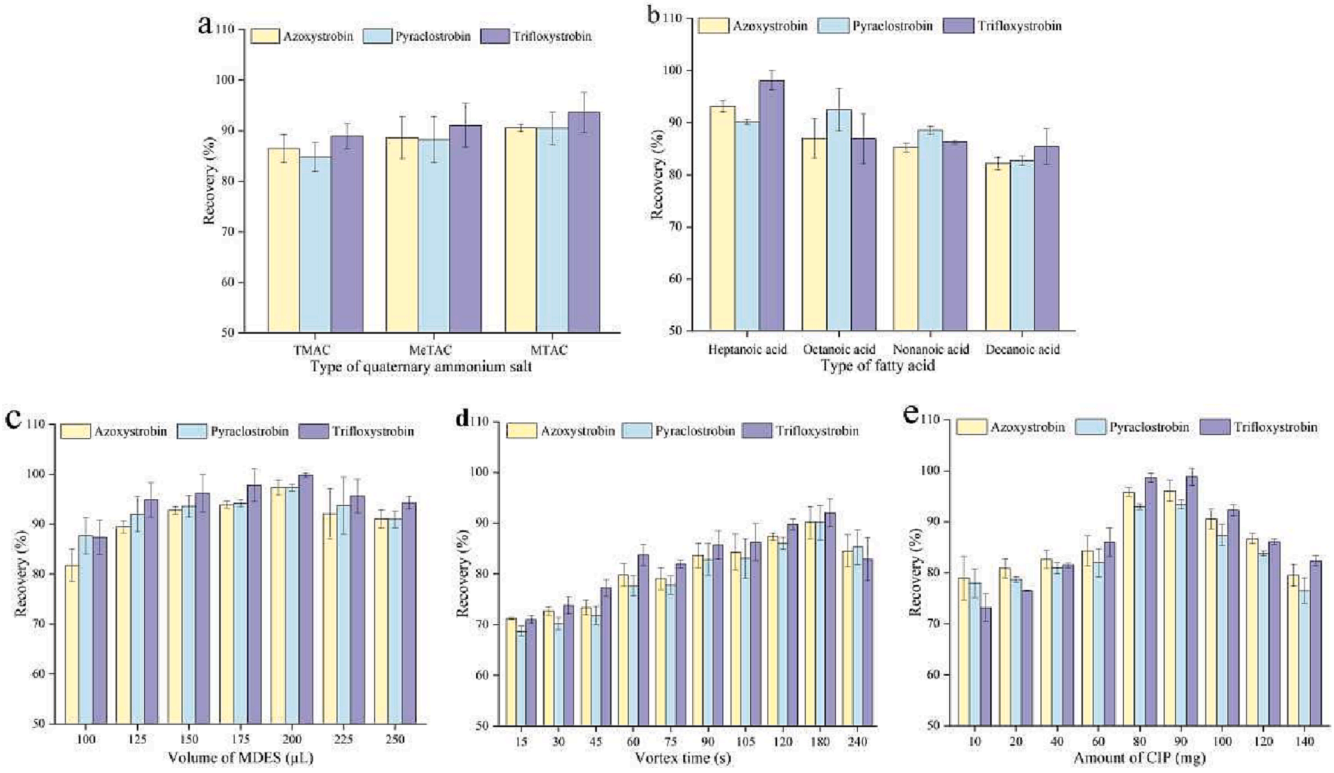

Fig. 3. Single factor optimization of the extraction conditions. (a: the effects of different types of quaternary ammonium salts. b: the effects of different types of fatty acids. c: the effects of different volumes of MDES. d: the effects of different vortex times. e: the effects of different amounts of CIP.).

3.2.1. Optimization of the type of MDESs

Suitable HBAs and HBDs can affect the physico-chemical properties of MDESs. In the hydrophobic MDESs, quaternary ammonium salts as HBAs should have long alkyl chains to exhibit a good affinity for strobilurin fungicides (Wang, Liu, Peng, & Ding, 2021). To get the best HBA, several quaternary ammonium salts (TMAC, MeTAC, and MTAC) containing long alkyl chains were investigated. Other invariable conditions were as follows: the HBD was heptanoic acid, the molar ratio of MDES was 0.5:0.08:6, the volume of MDES was 200 μL, the vortex time was 180 s, and the amount of CIP was 90 mg. In Fig. 3a, the ER of strobilurin fungicides gradually increased with the increase in the alkyl chain length. MeTAC and TMAC have shorter alkyl chains and demonstrate stronger hydrophilicity than MTAC, resulting in greater instability of MDESs in the hydrophilic sample and weaker affinity to hydrophobic strobilurin fungicides (Mokhodoeva, Maksimova, Shishov, & Shkinev, 2023). Therefore, MTAC was chosen as the HBA.

The length of the carbon chain of fatty acids as HBDs influences the ER (Chen, Huang, Hung, Chen, Lin, & Yang, 2021). To obtain optimal HBD, fatty acids (heptanoic acid, octanoic acid, nonanoic acid, and decanoic acid) with different carbon chain lengths were investigated. Other invariable conditions were as follows: the HBA was MTAC, the molar ratio of MDES was 0.5:0.08:6, the volume of MDES was 200 μL, the vortex time was 180 s, and the amount of CIP was 90 mg. In Fig. 3b, the ER of strobilurin fungicides gradually decreased with the increase in the carbon chain of fatty acids. Heptanoic acid provided higher diffusion coefficients and more effective mass transfer due to lower viscosity in comparison with octanoic acid, nonanoic acid, and decanoic acid (Shishov, Pochivalov, Dubrovsky, & Bulatov, 2023). Therefore, heptanoic acid was chosen as the HBD.

3.2.2. Optimization of the volume of MDES

In the extraction process, the appropriate volume of MDES not only improves the recovery but also enhances the response, however, excess MDES may reduce the sensitivity due to the dilution effect (Faraji, 2019). To determine the optimal MDES volume, different volumes (100, 125, 150, 175, 200, 225, and 250 μL) of MDESs were investigated. Other invariable conditions were as follows: the HBA was MTAC, the HBD was heptanoic acid, the molar ratio of MDES was 0.5:0.08:6, the vortex time was 180 s, and the amount of CIP was 90 mg. In Fig. 3c, the ER of strobilurin fungicides gradually increased and then decreased with the increase in the volume of MDES. An insufficient volume of MDES can lead to insufficient extraction and collection difficulty, while the excessive volume of MDES may affect the vortex effect (Mostafa, Shaaban, Alqarni, Alghamdi, Alsultan, Saleh Al-Saeed, et al., 2022). When the volume of MDES was 200 μL, the ER was the highest. Therefore, the volume of MDES of 200 μL was chosen.

3.2.3. Optimization of the vortex time

Vortex is formed as a result of intense fluid agitation, which breaks down extraction solvents into tiny droplets to increase the contact area between extraction solvents and sample solution. Hence, the vortex promotes the equilibration and distribution of the target analytes in the MDES and aqueous solution, which was affected by the vortex time (Bai, Zhang, Zhang, Hou, Niu, Hu, et al., 2021). To replace toxic dispersants to help disperse and effectively achieve the phase balance of target analytes between the MDES and the sample solution, different vortex times (15, 30, 45, 60, 75, 90, 105, 120, 180, and 240 s) were investigated. Other invariable conditions were as follows: the HBA was MTAC, the HBD was heptanoic acid, the molar ratio of MDES was 0.5:0.08:6, the volume of MDES was 200 μL, and the amount of CIP was 90 mg. In Fig. 3d, the ER of strobilurin fungicides gradually increased and then decreased with the increase in the vortex time. Theoretically, the increase of vortex time could accelerate the transfer of target analytes to the MDES phase. Nonetheless, the ER descended after 180 s, possibly due to the loss of the MDES phase (Elencovan, Joseph, Yahaya, Abdul Samad, Raoov, Lim, et al., 2022). Therefore, considering the ER and time, the vortex time of 180 s was chosen.

3.2.4. Optimization of the amount of CIP

CIP can enhance the magnetic force of magnetic solvents and reduce the magnetic separation time (Piao, Jiang, Qin, Ma, Sun, Wang, et al., 2021). To obtain the optimal amount of CIP, different amounts (10, 20, 40, 60, 80, 90, 100, 120, and 140 mg) of CIP were investigated. Other invariable conditions were as follows: the HBA was MTAC, the HBD was heptanoic acid, the molar ratio of MDES was 0.5:0.08:6, the volume of MDES was 200 μL, and the vortex time was 180 s. In Fig. 3e, the ER of strobilurin fungicides gradually increased, then decreased with the increase in the amount of CIP (perhaps because collection of the extractant phase was not completed when an inadequate CIP was added); however, when an excess of CIP was added, the extractant phase overabundantly adhered to the CIP, resulting in loss during filtration (Jing, Xue, Sang, Wang, & Jia, 2022). When the amount of CIP was 90 mg, the ER was the highest, therefore, 90 mg of CIP was chosen.

3.3. Evaluation of the method

To validate the method performance, the linear equations, coefficient of determination (R^2), limit of detection (LOD), limit of quantification (LOQ), intra-day and inter-day relative standard deviations (RSDs) were evaluated (Table 1). These implied that strobilurin fungicides had a good linear relationship in the range of 0.1–10 mg L^{-1}, with $R^2 > 0.996$. The LODs calculated from a signal-to-noise ratio (SNR) of 3 were in the range of 0.001–0.002 mg L^{-1}, while the LOQs calculated from a SNR of 10 were in the range of 0.003–0.008 mg L^{-1}. The intra-day and inter-day RSDs were 1.7–5.5% and 4.4–7.9% ($n = 5$). Matrix effects were accessed by comparing the slopes of the calibration curves, and the results showed that matrix effects are considered tolerable because they are between 80% and 120% (Table 1). The results indicated that good sensitivity and repeatability could be obtained using the established method.

3.4. Real sample analysis

The applicability of the proposed method to real samples was evaluated by studying water, juice, and vinegar samples under optimal conditions. The residue of strobilurin fungicides in real samples was lower than the LODs. Thus, the spiked samples with different concentrations (0.1, 1, and 10 mg L^{-1}) were prepared, and the spiked recovery experiment was repeated three times for each concentration. The experimental results showed that the spiked recoveries in the real samples were 81.9–108.9%, and the RSDs were 1.2–4.5% (Table 2). Therefore, the method demonstrates good accuracy and applicability and can thus be used to detect strobilurin fungicides in food samples.

3.5. Comparison with other methods

This method was compared with reported DLLME studies (Ahmadi-Jouibari, Shaahmadi, Moradi, & Fattahi, 2022; Huang, Du, Wu, Jia, Wang, & Jing, 2020; Jia, Huang, Zhao, Wang, & Jing, 2020; Toloza, Almeida, Silva, Macedo, Lamounier, Aucelio, et al., 2020) by comparing the extraction methods, extractant solvents, dispersant solvents, centrifugation, ice baths, dryness, dissolution, detection methods, LODs, and ER values (Table 3). Compared with other studies, this method used green MDES as an extractant solvent to replace toxic extractants (such as carbon tetrachloride). The toxic dispersants (such as acetonitrile and acetone) were not used. In addition, the time-consuming steps (centrifugation, ice bath, dryness, and redissolution) could be avoided. Satisfactory LOQs and ER values were obtained. Therefore, the developed MDES-DLLME-HPLC was a rapid, green method for detecting strobilurin fungicides.

Table 1
Performance of the MDES-DLLME method.

Analyte	Sample	Linear equation	R^2	LOD (mg L^{-1})	LOQ (mg L^{-1})	Intra-day RSD (%) ($n = 5$)	Inter-day RSD (%) ($n = 5$)	Matrix effect (%)
Azoxystrobin	Water	$y = 575.34x + 86.239$	0.999	0.002	0.008	3.2	4.4	101.4
	Juice	$y = 671.97x + 29.041$	0.999	0.001	0.004	3.3	4.7	118.4
	Vinegar	$y = 536.92x + 63.725$	0.996	0.001	0.004	5.5	5.8	94.6
Pyraclostrobin	Water	$y = 1391.2x + 18.304$	0.999	0.001	0.004	1.7	4.4	91.7
	Juice	$y = 1553.9x + 110.30$	0.999	0.001	0.003	2.8	6.2	102.4
	Vinegar	$y = 1481.7x + 101.57$	0.999	0.001	0.003	3.4	7.9	97.7
Trifloxystrobin	Water	$y = 1023.5x + 93.995$	0.999	0.001	0.005	3.2	5.0	96.1
	Juice	$y = 1055.5x + 63.757$	0.999	0.001	0.005	3.1	5.3	99.1
	Vinegar	$y = 1036.9x + 104.18$	0.999	0.001	0.005	2.6	6.0	97.4

Table 2
Analysis of strobilurin fungicides in real samples.

Analyte	Concentration (mg L^{-1})	Water		Juice		Vinegar	
		ER (%)	RSD (%)	ER (%)	RSD (%)	ER (%)	RSD (%)
Azoxystrobin	0	–	–	–	–	–	–
	0.1	86.7	1.2	87.1	4.2	88.8	1.3
	1	97.2	1.2	95.7	3.5	88.6	2.9
	10	95.8	2.5	108.9	1.3	98.8	4.1
Pyraclostrobin	0	–	–	–	–	–	–
	0.1	99.7	1.6	96.0	2.7	96.2	4.3
	1	94.9	3.1	97.7	1.8	86.6	1.2
	10	99.6	2.3	90.5	2.3	106.9	2.3
Trifloxystrobin	0	–	–	–	–	–	–
	0.1	94.3	2.7	102.1	1.8	97.9	2.5
	1	97.7	1.7	97.0	2.3	88.1	1.9
	10	93.4	2.9	81.9	2.0	92.3	4.5

Table 3
Comparisons of the proposed DLLME with other DLLME methods of strobilurin fungicides.

Analyte	Extraction method	Extractant solvent	Dispersion solvent	Centrifugation	Ice bath	Dryness & redissolution	Detection method	LOD (mg L^{-1})	ER (%)	Reference
Kresoxim-methyl	DLLME	CCl_4	Acetonitrile (2000 μL)	3000 rpm (20 min)	–	√	HPLC-FLD	0.0190–0.0650	80.0–101.0	(Toloza, et al., 2020)
Azoxystrobin Pyraclostrobin Trifloxystrobin	DLLME	$C_8H_{17}COOH$	Acetonitrile (600 μL)	4000 rpm (5 min)	√	–	HPLC-DAD	0.0026–0.0049	82.0–93.2	(Huang, Du, Wu, Jia, Wang, & Jing, 2020)
Azoxystrobin Pyrimethanil Kresoxim-methyl	DLLME	DES	Acetone (1000 μL)	5000 rpm (3 min)	√ (3 min)	–	HPLC-UV	0.0015–0.0020	76.0–92.0	(Ahmadi-Jouibari, Shaahmadi, Moradi, & Fattahi, 2022)
Picoxystrobin Pyraclostrobin Trifloxystrobin	DLLME	DES	$NH_3{\cdot}H_2O$ (50 μL) $NaHCO_3$ (10 mg) Citric acid (80 mg)	4000 rpm (5 min)	√ (15 min)	–	HPLC-DAD	0.0002–0.0004	77.4–106.9	(Jia, Huang, Zhao, Wang, & Jing, 2020)
Azoxystrobin Pyraclostrobin Trifloxystrobin	DLLME	MDES	–	–	–	–	HPLC-DAD	0.0010–0.0020	81.9–108.9	This method

4. Conclusion

In this study, a green hydrophobic MDES replaced toxic extractants, vortex-assisted dispersion excluded toxic dispersants, and magnetic separation avoided otherwise time-consuming centrifugation. The method showed satisfactory accuracy, precision, and sensitivity. This rapid, green method was successfully applied to the detection of strobilurin fungicides in food samples using HPLC. There are few types of hydrophobic MDESs reported, so more hydrophobic MDESs with a strong affinity for specific hydrophobic compounds should be developed in the future.

CRediT authorship contribution statement

Min Wang: Methodology, Investigation, Writing – original draft. **Luyao Zhao:** Data curation. **Yu Niu:** Software. **Shu Qin:** Formal

analysis. **Lixin Zhang:** Validation. **Liyan Jia:** Project administration. **Xu Jing:** Conceptualization, Methodology.

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.

Data availability

Data will be made available on request.

Acknowledgments

This study was supported by the National Natural Science Foundation of China [grant number 32202161]; Shanxi Province Key R&D Plan [grant number 202102140601018]; Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi [grant number 2021L163]; and Transformation of Scientific and Technological Achievements Programs of Higher Education Institutions in Shanxi.

Informed consent

Not applicable.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2023.100711.

References

Ahmadi-Jouibari, T., Shaahmadi, Z., Moradi, M., & Fattahi, N. (2022). Extraction and determination of strobilurin fungicides residues in apple samples using ultrasound-assisted dispersive liquid-liquid microextraction based on a novel hydrophobic deep eutectic solvent followed by HPLC-U.V. *Food Additives and Contaminants Part a-Chemistry Analysis Control Exposure & Risk Assessment, 39*, 105–115. https://doi.org/10.1080/19440049.2021.1978559

Babaee, S., & Daneshfar, A. (2018). Magnetic deep eutectic solvent-based ultrasoundassisted liquid-liquid microextraction for determination of hexanal and heptanal in edible oils followed by gas chromatography-flame ionization detection. *Analytical Methods, 10*, 4162–4169. https://doi.org/10.1039/c8ay01058g

Bai, Y.-E., Zhang, X.-T., Zhang, R.-M., Hou, J., Niu, Y.-J., Hu, S., & Gao, J.-P. (2021). Simultaneous determination of lobetyolin and atractylenolide III in Codonopsis Radix by dispersive liquid-liquid microextraction based on hydrophobic deep eutectic solvent. *Microchemical Journal, 170*. https://doi.org/10.1016/j.microc.2021.106664

Chen, C. C., Huang, Y. H., Hung, S. M., Chen, C. Y., Lin, C. W., & Yang, H. H. (2021). Hydrophobic deep eutectic solvents as attractive media for low-concentration hydrophobic VOC capture. *Chemical Engineering Journal, 424*, Article 130420. https://doi.org/10.1016/j.cej.2021.130420

El Achkar, T., Greige-Gerges, H., & Fourmentin, S. (2021). Basics and properties of deep eutectic solvents: A review. *Environmental Chemistry Letters, 19*, 3397–3408. https://doi.org/10.1007/s10311-021-01225-8

Elencovan, V., Joseph, J., Yahaya, N., Abdul Samad, N., Raoov, M., Lim, V., & Zain, N. N. M. (2022). Exploring a novel deep eutectic solvents combined with vortex assisted dispersive liquid-liquid microextraction and its toxicity for organophosphorus pesticides analysis from honey and fruit samples. *Food Chemistry, 368*, 130835. https://doi.org/10.1016/j.foodchem.2021.130835.

Faraji, M. (2019). Determination of some red dyes in food samples using a hydrophobic deep eutectic solvent-based vortex assisted dispersive liquid-liquid microextraction coupled with high performance liquid chromatography. *Journal of Chromatography A, 1591*, 15–23. https://doi.org/10.1016/j.chroma.2019.01.022

Farajzadeh, M. A., Kiavar, L., & Pezhhanfar, S. (2021). Development of a method based on dispersive liquid-liquid microextraction followed by partial vaporization of the extract for ultra-preconcentration of some pesticide residues in fruit juices. *Journal of Chromatography A, 1653*, Article 462427. https://doi.org/10.1016/j.chroma.2021.462427

Farooq, M. Q., Tryon-Tasson, N., Biswas, A., & Anderson, J. L. (2022). Preparation of ternary hydrophobic magnetic deep eutectic solvents and an investigation into their physicochemical properties. *Journal of Molecular Liquids, 365*, Article 120000. https://doi.org/10.1016/j.molliq.2022.120000

Ghasemi, R., Mirzaei, H., Mogaddam, M. R. A., Khandaghi, J., & Javadi, A. (2022). Application of magnetic ionic liquid-based air–assisted liquid–liquid microextraction followed by back-extraction optimized with centroid composite design for the extraction of antibiotics from milk samples prior to their determination by HPLC–DAD. *Microchemical Journal, 181*, Article 107764. https://doi.org/10.1016/j.microc.2022.107764

Huang, X., Du, Z. Y., Wu, B. Q., Jia, L. Y., Wang, X. W., & Jing, X. (2020). Dispersive liquid-liquid microextraction based on the solidification of floating organic droplets for HPLC determination of three strobilurin fungicides in cereals. *Food Additives and Contaminants Part a-Chemistry Analysis Control Exposure & Risk Assessment, 37*, 1279–1288. https://doi.org/10.1080/19440049.2020.1758349

Hussin, S. A. M., Varanusupakul, P., Kassim, M. A., Rozi, S. K. M., & Mohamad, S. (2021). Vortex assisted dispersive liquid-liquid microextraction based on low transition temperature mixture solvent for the HPLC determination of pyrethroids in water samples: Experimental study and COSMO-RS. *Microchemical Journal, 171*, Article 106780. https://doi.org/10.1016/j.microc.2021.106780

Jia, L. Y., Huang, X., Zhao, W. F., Wang, H. H., & Jing, X. (2020). An effervescence tablet-assisted microextraction based on the solidification of deep eutectic solvents for the determination of strobilurin fungicides in water, juice, wine, and vinegar samples by HPLC. *Food Chemistry, 317*, Article 126424. https://doi.org/10.1016/j.foodchem.2020.126424

Jing, X., Huang, X., Zhang, Y. M., Wang, M., Xue, H. Y., Wang, X. W., & Jia, L. Y. (2022). Cyclodextrin-based dispersive liquid-liquid microextraction for the determination of fungicides in water, juice, and vinegar samples via HPLC. *Food Chemistry, 367*, Article 130664. https://doi.org/10.1016/j.foodchem.2021.130664

Jing, X., Xue, H. Y., Sang, X. Y., Wang, X. W., & Jia, L. Y. (2022). Magnetic deep eutectic solvent-based dispersive liquid-liquid microextraction for enantioselectively determining chiral mefentrifluconazole in cereal samples via ultra-high-performance liquid chromatography. *Food Chemistry, 391*, Article 133220. https://doi.org/10.1016/j.foodchem.2022.133220

Khezeli, T., & Daneshfar, A. (2017). Synthesis and application of magnetic deep eutectic solvents: Novel solvents for ultrasound assisted liquid-liquid microextraction of thiophene. *Ultrasonics Sonochemistry, 38*, 590–597. https://doi.org/10.1016/j.ultsonch.2016.08.023

Kovacevic, M., Hackenberger, D. K., & Hackenberger, B. K. (2021). Effects of strobilurin fungicides (azoxystrobin, pyraclostrobin, and trifloxystrobin) on survival, reproduction and hatching success of Enchytraeus crypticus. *Science of the Total Environment, 790*, Article 148143. https://doi.org/10.1016/j.scitotenv.2021.148143

Lemos, V. A., Barreto, J. A., Santos, L. B., de Assis, R. D., Novaes, C. G., & Cassella, R. J. (2022). In-syringe dispersive liquid-liquid microextraction. *Talanta, 238*, Article 123002. https://doi.org/10.1016/j.talanta.2021.123002

Liu, T., Hu, Y., Feng, Y., Liu, Y., Xie, P., Chai, L., … Cao, X. (2022). Preparation of metal-organic framework @molecularly imprinted polymers for extracting strobilurin fungicides from agricultural products. *Journal of Chromatography B, 1209*, Article 123427. https://doi.org/10.1016/j.jchromb.2022.123427

Mokhodoeva, O., Maksimova, V., Shishov, A., & Shkinev, V. (2023). Separation of platinum group metals using deep eutectic solvents based on quaternary ammonium salts. *Separation and Purification Technology, 305*, Article 122427. https://doi.org/10.1016/j.seppur.2022.122427

Monajemzadeh, F., Mohebbi, A., Farajzadeh, M. A., Nemati, M., & Mogaddam, M. R. A. (2021). Dispersive solid phase extraction combined with in syringe deep eutectic solvent based dispersive liquid-liquid microextraction for determination of some pesticides and their metabolite in egg samples. *Journal of Food Composition and Analysis, 96*, Article 103696. https://doi.org/10.1016/j.jfca.2020.103696

Mostafa, A., Shaaban, H., Alqarni, A. M., Alghamdi, M., Alsultan, S., Saleh Al-Saeed, J., … Ahmad, R. (2022). Vortex-assisted dispersive liquid–liquid microextraction using thymol based natural deep eutectic solvent for trace analysis of sulfonamides in water samples: Assessment of the greenness profile using AGREE metric, GAPI and analytical eco-scale. *Microchemical Journal, 183*, Article 107976. https://doi.org/10.1016/j.microc.2022.107976

Nemati, M., Farajzadeh, M. A., Mogaddam, M. R. A., Mohebbi, A., Azimi, A. R., Fattahi, N., & Tuzen, M. (2022). Development of a gas-controlled deep eutectic solvent-based evaporation-assisted dispersive liquid-liquid microextraction approach for the extraction of pyrethroid pesticides from fruit juices. *Microchemical Journal, 175*, Article 107196. https://doi.org/10.1016/j.microc.2022.107196

Nian, B., & Li, X. (2022). Can deep eutectic solvents be the best alternatives to ionic liquids and organic solvents: A perspective in enzyme catalytic reactions. *International Journal of Biological Macromolecules, 217*, 255–269. https://doi.org/10.1016/j.ijbiomac.2022.07.044

Omar, K. A., & Sadeghi, R. (2022). Physicochemical properties of deep eutectic solvents: A review. *Journal of Molecular Liquids, 360*, Article 119524. https://doi.org/10.1016/j.molliq.2022.119524

Piao, H. L., Jiang, Y. X., Qin, Z. C., Ma, P. Y., Sun, Y., Wang, X. H., … Fei, Q. (2021). Application of an in-situ formulated magnetic deep eutectic solvent for the determination of triazine herbicides in rice. *Talanta, 222*, Article 121527. https://doi.org/10.1016/j.talanta.2020.121527

Psillakis, E. (2019). Vortex-assisted liquid-liquid microextraction revisited. *Trac-Trends in Analytical Chemistry, 113*, 332–339. https://doi.org/10.1016/j.trac.2018.11.007

Qiao, L., Tao, Y., Yao, W., Zhao, J., & Yan, Y. (2022). A magnetic ionic liquid based vortex-assisted dispersive liquid-liquid microextraction coupled with back-extraction for the enrichment of fluoroquinolone antibiotics. *Journal of Pharmaceutical and Biomedical Analysis, 219*, Article 114903. https://doi.org/10.1016/j.jpba.2022.114903

Rezaee, M., Assadi, Y., Milani Hosseini, M.-R., Aghaee, E., Ahmadi, F., & Berijani, S. (2006). Determination of organic compounds in water using dispersive liquid-liquid microextraction. *Journal of Chromatography A, 1116*, 1–9. https://doi.org/10.1016/j.chroma.2006.03.007

Sadeghi, M., Tehrani, M. S., & Faraji, H. (2022). Vortex-assisted liquid-liquid microextraction for the trace determination of potassium bromate in flour food

products. *Food Chemistry, 378*, Article 132109. https://doi.org/10.1016/j.foodchem.2022.132109

Shishov, A., Pochivalov, A., Dubrovsky, I., & Bulatov, A. (2023). Deep eutectic solvents with low viscosity for automation of liquid-phase microextraction based on lab-in-syringe system: Separation of Sudan dyes. *Talanta, 255*. https://doi.org/10.1016/j.talanta.2022.124243

Song, X. Y., Li, F. Y., Yan, T., Tian, F., Ren, L. L., Jiang, C. F., … Zhang, S. S. (2022). Research progress in the sample pretreatment techniques and advanced quick detection methods of pesticide residues. *Process Safety and Environmental Protection, 165*, 610–622. https://doi.org/10.1016/j.psep.2022.07.047

Toloza, C. A. T., Almeida, J. M. S., Silva, L. O. P., Macedo, R. C., Lamounier, A. P., Aucelio, R. Q., & da Cunha, A. (2020). Determination of kresoxim-methyl in water and in grapes by high-performance liquid chromatography (HPLC) using photochemical-induced fluorescence and dispersive liquid-liquid microextraction (DLLME). *Analytical Letters, 53*, 2202–2221. https://doi.org/10.1080/00032719.2020.1733589

Wang, X. L., Liu, M., Peng, F. X., & Ding, X. Q. (2021). Hydrophobic magnetic deep eutectic solvent: Synthesis, properties, and application in DNA separation. *Journal of Chromatography A, 1659*, Article 462626. https://doi.org/10.1016/j.chroma.2021.462626

Yao, T., & Du, K. F. (2020). Simultaneous determination of sulfonamides in milk: In-situ magnetic ionic liquid dispersive liquid-liquid microextraction coupled with HPLC. *Food Chemistry, 331*, Article 127342. https://doi.org/10.1016/j.foodchem.2020.127342

Zhang, C., Zhou, T. T., Xu, Y. Q., Du, Z. K., Li, B., Wang, J. H., … Zhu, L. S. (2020). Ecotoxicology of strobilurin fungicides. *Science of the Total Environment, 742*, Article 140611. https://doi.org/10.1016/j.scitotenv.2020.140611

Zhang, J., Li, S., Yao, L., Yi, Y., Shen, L., Li, Z., & Qiu, H. (2022). Responsive switchable deep eutectic solvents: A review. *Chinese Chemical Letters*. , Article 107750. https://doi.org/10.1016/j.cclet.2022.107750

Zhao, R. Y., An, J., Sun, Y. M., He, L. J., Jiang, X. M., & Zhang, S. S. (2021). A simple and low-cost sample preparation for the effective extraction, purification and enrichment of aflatoxins in wheat by combining with ionic liquid-based dispersive liquid-liquid microextraction. *Microchemical Journal, 164*, Article 106036. https://doi.org/10.1016/j.microc.2021.106036