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ORIGINAL RESEARCH PAPER

Application of ultrasound-assisted deep eutectic solvent extraction combined with liquid-liquid extraction method to the extraction of three pesticide residues from fruit and vegetable samples

SUE CHEN, QI AN, HONG SUN, and MENGQIAN MAO*

Department of Pharmacy, Shanxi Health Vocational College, Jinzhong, Shanxi Province, 030619, PR China

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ABSTRACT

A simple, inexpensive and sensitive method was developed for the simultaneous determination of three pesticide residues (carbendazim, thiophanate-methyl, and imidacloprid) in fruit and vegetable samples using high performance liquid chromatography (HPLC) based on a combined pretreatment of ultrasound-assisted deep eutectic solvent extraction (UA-DES-E) and liquid-liquid extraction (LLE). In this study, various types of deep eutectic solvents (DESs) were synthesized and the extraction efficiency was compared as extraction solvents. Results showed that glycerol-proline = 9:4 (GP-5) obtained the highest extraction efficiency among different types of DESs. Experiment conditions, including DES volume, extraction time and pH, were systematically optimized using single-factor experiment. Under the optimum conditions, the limits of detection (LODs) and quantification (LOQs) were in the ranges of 0.05–0.2 $\mu\text{g} \cdot \text{mL}^{-1}$ and 0.1–0.5 $\mu\text{g} \cdot \text{mL}^{-1}$, respectively. The relative recoveries of the three pesticides in the fruit and vegetable samples ranged from 85.7 to 113.0% at two spiked levels. Meanwhile, the method achieved excellent linearity with determination coefficients (r) greater than 0.999. Furthermore, the method was successfully applied to the analysis of the pesticides in real fruit and vegetable samples (apple, tomato, and grape).

KEYWORDS

deep eutectic solvents, pesticide residue, ultrasound-assisted extraction, liquid-liquid extraction, fruit and vegetable samples

INTRODUCTION

Pesticides are a unique group of synthetically chemicals designed to protect agricultural products from diseases caused by fungus, pests, and herbs, they have been extensively used in agricultural production to prevent or reduce losses and consequently improve product quality. Among the various pesticides widely used in fruit and vegetable, the most commonly used broad-spectrum fungicides are carbendazim (CA), thiophanate-methyl (TH) and imidacloprid (IM) [1]. Although these pesticides have significantly improved the yield of products and benefited people, the extensive use of pesticides can cause environmental pollution [2]. Meanwhile, the presence of pesticide residues and their metabolites can potentially affect human health through the food chain [3], the side effects on human health include acute neurologic toxicity, chronic neurodevelopment impairment, and endocrine systems or cancer [4]. Therefore, many countries and organizations have established regulations to control the maximum residue limits for these pesticides in different agricultural and sideline products. The U.S. has promulgated Title 40 CFR (the code of Federal

*Corresponding author. Tel.: +86 15581752358.
E-mail: m13125542928@163.com

Regulation) Part 180 to regulate the maximum allowable pesticide content in food. In China, the national standard GB2763-2019 will be implemented to control pesticide residues in February 15, 2020. To meet the updating standards requirements, it is significant to develop a rapid, reliable, and inexpensive pretreatment method to monitor the residue of pesticides in agricultural products.

Effective sample pretreatment procedure for extraction and purification is essential prior to analysis as pesticides occur in complicated matrices. At present, several pretreatment techniques such as supercritical fluid extraction (SFE) [5], accelerated solvent extraction (ASE) [6] and, matrix solid phase dispersion (MSPD) [7] and QuEChERS [14] are frequently and traditionally used for extraction of pesticides from fruits and vegetables. SFE is an extraction technology that utilizing the strong solubility of Supercritical Fluid (SCF), which has the dual characteristics as it is in a critical state between gas and liquid. This technology has higher extraction efficiency, but substantial investment in equipment and laborious selection of entrainers limited its development [8]. ASE method extracts solid or semisolid samples with liquid solvents under high temperature (50–200 °C) and pressure (6.9–20.7 MPa) [9]. High temperature and pressure of solvent increase the ability of solubilizing the analyte, therefore, this technology shows good extraction results in the analysis of residual pesticides in food [10]. However, ASE suffers from the disadvantage of its complicated operation. Combination of extraction, fractionation, and clean-up into a single step is the main characteristic of MSPD, and so far this method was successfully applied to the extraction of solid, semisolid and liquid matrices [11]. There are still some shortcomings in MSPD such as unsatisfactory purification effect, limited pesticide types or matrix type. Although these methods have been applied widely, they all have their own shortcomings. Ultrasound-assisted extraction (UAE) is a common extraction method that has been used as an alternative to conventional methods in the extraction of food products [12]. UAE techniques speed up the mass transfer of analytes through increasing the interaction between solvents and matrix [13], but the extraction effect is general. Therefore, finding new solvents with better selectivity could be future innovative direction in UAE application of extraction. The QuEChERS method, short for quick-easy-cheap-effective-rugged-safe, has been the universal measure worldwide for pesticide multiresidue analysis [14–16]. QuEChERS method consists of solid-liquid extraction, salting out and cleaning with dispersive sorbents [17]. A sample prepared for pesticide analysis by QuEChERS expends as little as 30 min in average [18]. QuEChERS can significantly reduce the use of solvent and sample preparation steps. However, precision instrument (e.g., LC-MS) is required for detection generally.

Much attention has been paid towards using green solvents as a replacement for organic solvents due to a large number of traditional organic solvents which are toxic and not environmentally friendly have been used during the extraction process. In recent years, although ionic liquid solvents (ILs) have attracted much attention and are widely

used as sustainable alternatives to hazardous organic solvents because of their unique properties such as low melting temperature, high thermal stability, wide liquid phase range, non-flammability, and low vapor pressure [19], it still shows drawbacks such as toxic, complicated and costly synthesis process [20]. Deep eutectic solvents (DESs), a green and new type of ILs, which have similar physicochemical properties to ILs, have emerged [21]. It was first introduced by Abbott et al. in 2003 [22]. DESs are formed by combining two or more components from hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs) with a lower melting point than that of its individual components mainly due to the generation of inter molecular hydrogen bonds and Van der Waals interactions [23]. In comparison with ILs, DESs have numerous advantages, such as low cost, chemical inertness with water, easy preparation and environmental friendliness [24]. Compared with QuEChERS, DESs provided several same advantages, such as simplicity of experimental steps, low expending and low toxicity solvents. However, most DESs could be prepared with natural compounds with certain molar ratios, which express these new extraction solvent are more environmentally friendly. Most of DESs are liquid at room temperature [25]. Due to the attractive properties of DES, they have been extensively used in catalysis [26], organic synthesis [27], dissolution [28], electrochemistry [29], etc. Nevertheless, the application of DESs as effective solvents to extract pesticides from food was rarely. For instance, Jouyban [30] developed a new method using DES for the extraction and preconcentration of different classes of pesticides from food samples. Farajzadeh [31] established a temperature-controlled liquid phase microextraction using DES for the extraction and preconcentration of diazinon, metalaxyl, bromopropylate, oxadiazon, and fenazaquin pesticides from fruit juice and vegetable samples. However, in these studies, expensive tandem mass spectrometry instruments are often required and the process is relatively cumbersome and cannot be widely applied to the determination of selected target analytes. In general, liquid phase chromatograph is typically used for the determination of selected pesticides. Therefore, it is a very significant work to use DES as the extraction solvent to extract pesticides from food matrix samples instead of using traditional organic solvents.

Since the amount of pesticides in food samples is traceable, a purification and preconcentration step is necessary before determination of analytes by chromatographic methods. Liquid-liquid extraction (LLE) [32], solid-phase extraction (SPE) [33] and dispersive-solid-phase extraction (DSPE) [34] are the most common techniques employed in the treatment of different samples. Among them, LLE is a simple, convenient and widely applicable method for the purification and preconcentration of analytes from aqueous matrices [35]. However, LLE requires a generous amount of samples and organic solvents. To overcome these shortcomings in LLE, in this study, DESs was combined to LLE method for purifying the preliminary extracts.

In this study, we aimed to develop an efficient ultrasound-assisted deep eutectic solvent extraction (UA-DES-E)

pretreatment method for the extraction of three frequently used pesticides from fruit and vegetable samples. LLE method was used for purification and preconcentration, and high performance liquid chromatography (HPLC) method was developed to simultaneously separate and quantify the target pesticides. The proposed method has the advantages of simplicity in operation, high extraction recoveries and environmental-friendly. DESs obtained under different preparation conditions and ratios were used to study the extraction efficiency of target pesticides. The interactions between the DESs and target pesticides were analyzed, and the optimal conditions for extraction and determination by HPLC were found. Under the optimized conditions, the proposed method was validated for analyzing three different fruit and vegetable samples.

EXPERIMENTAL

Chemicals and solutions

The selected three pesticides standards of carbendazim (CA, 99%), thiophanate-methyl (TH, 99%) and imidacloprid (IM, 99%) were purchased from Shanghai Aladdin Chemistry Co., Ltd. (Shanghai, China). A stock solution of pesticides ($100 \text{ mg} \cdot \text{L}^{-1}$ of each pesticide) was prepared by dissolving an appropriate amount of each pesticide in methanol and stored at 4°C . Their chemical structures are shown in Fig. 1.

Choline chloride (98.0%) and proline (99.0%) were from Bailingwei Technology Co., Ltd. (Beijing, China). Glycerol (99.0%), 1,4-butanediol (98.0%), urea (98.0%), lactic acid (98.0%), and oxalic acid (98.0%) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Ultrapure water was provided by Wahaha Group Co., Ltd. (Hangzhou, China). All chromatographic and analytical grade reagents were obtained from Yuwang Industrial Co., Ltd. (Shandong, China).

Apparatus

Quantitative analysis of the selected pesticides was performed on the Agilent HPLC 1100 system equipped with a degasser (G1322A), an autosampler (G1313A), a quat pump (G1311A), a column oven (G1316A), and a diode array detector (DAD, G1315B). (Agilent, San Jose, CA, USA).

Extraction and preconcentration method

Synthesis of DES. The DESs could be easily prepared by heating and stirring based on the previously reported procedure [36]. Accurately weighed components at proper

molar ratios and then mixed in a 50 mL glass vial, then the mixture was stirred at temperature of $60\sim 80^\circ\text{C}$ until a clear liquid was formed. The abbreviations of the DESs and their physical properties were shown in Table 1. The fourier-transform infrared (FT-IR) spectrum of pure proline, glycerol and synthesized DES of glycerol-proline (9:4) were shown in Fig. 2.

Sample preparation. The fruit and vegetable samples, including apple, tomato and grape were purchased from local supermarkets (Shanxi, China). After homogenization with a tissue mincer, the sample was frozen in a round bottom flask for 24 h and then dried by lyophilization. 0.5 g of homogenized sample was accurately weighed into a 10 mL centrifuge tube followed by addition of appropriate amount of extraction solvent (DES). The mixture was vortexed for 1 min and extracted in an ultrasonic bath (KQ-5200, Kunshan, China) at room temperature for 20 min to ensure the solvent well interacted with the sample and followed by centrifugation at 4,000 rpm for 5 min. The supernatant was transferred to another clean tube for further LLE procedure.

LLE procedure. During the LLE procedure, 1 mL of petroleum ether was added into the supernatant. Then the mixture was vortexed for 20 s and centrifuged at 4,000 rpm for 3 min to remove impurities other than the target analytes in the supernatant. After discarding the petroleum ether layer, the supernatant was re-extracted with 1 mL of dichloromethane, the target analytes were extracted into the dichloromethane layer. Then the dichloromethane layer was combined and dried by a gentle air stream at 50°C . Finally, the obtained residue was dissolved with certain amount of methanol, filtered through a $0.45 \mu\text{m}$ filter and injected into HPLC for further analysis.

Analytical method

Chromatographic separation was achieved on a Venusil MP C18 reversed-phase column ($250 \text{ mm} \times 4.6 \text{ mm}$, $5 \mu\text{m}$) within 20 min by HPLC. The column temperature was maintained at 30°C . The mobile phase consists of 0.05% (v/v) phosphoric acid aqueous water (A) and methanol (B) at a flow rate of $1.0 \text{ mL} \cdot \text{min}^{-1}$. Gradient elution program was 0–5 min, 90–40% A; 5–15 min, 40–20% A; 15–18 min, 20–10% A. The detection wavelength was set at 270 nm. The injection volume was 10 μL .

RESULTS AND DISCUSSION

Characterization of DES

DESs have a lower freezing point than their individual constituents, and this property is attributed to the reduction of the coulomb forces of DESs with the large volume and asymmetric charge distribution of molecular ions. The eutectic mixture resulted from intermolecular hydrogen bond between proline and glycerol. FT-IR is an attractive

Figure 1. Chemical structures of the three pesticides

Table 1. List of DESs synthesized in this study

Abbreviation	Component 1	Component 2	Mole ratio	Viscosity Pa·s	Conductivity $\mu\text{S}\cdot\text{cm}^{-1}$	Density $\text{g}\cdot\text{cm}^{-3}$	References
ChGly	Choline chloride	Glycerol	1:2	0.177	1,647	1.1854	[37]
ChBu	Choline chloride	1,4-butanediol	1:4	0.047	2,430	1.0410	[37]
ChLa	Choline chloride	Lactic acid	1:2	–	–	–	
ChOx	Choline chloride	Oxalic acid	1:1	0.089	2,350	1.2371	[37]
ChUr	Choline chloride	Urea	1:2	0.214	1,287	1.1879	[37]
GP-4	Glycerol	Proline	7:4	–	–	–	
GP-5	Glycerol	Proline	9:4	–	–	–	
GP-6	Glycerol	Proline	11:4	–	–	–	

method for obtaining hydrogen bond information [38]. Therefore, we investigated FT-IR spectra of pure proline (Fig. 2(A)), glycerol (Fig. 2(B)), and synthesized GP-5 (Fig. 2(C)) to confirm the formation of hydrogen bond. It was expected that the wavelength of the O–H group would be altered in the DES compared to in the pure proline and glycerol.

Absorption bands in the FT-IR spectra are mainly caused by changes between different vibrational states of bonds in molecules [38]. The N–H, C–H, and C–N vibration of pure proline are positioned at $3,426.7\text{ cm}^{-1}$, $2,983.2\text{ cm}^{-1}$, and $1,169.7\text{ cm}^{-1}$ in Fig. 2(A). In the FT-IR spectra, the characteristic peaks presented at $3,383.1\text{ cm}^{-1}$, $2,937.3\text{ cm}^{-1}$, and $1,041.6\text{ cm}^{-1}$ belong to O–H, C–H, and C–O vibration of pure glycerol displayed in Fig. 2(B), respectively. The FT-IR spectra of GP-5 were shown in Fig. 2(C). According to the FT-IR spectrum of GP-5, the stretching vibration absorption peaks of $\nu_{\text{O-H}}$ in glycerol shift from $3,383.1\text{ cm}^{-1}$ to $3,373.1\text{ cm}^{-1}$ in prepared GP-5 because a portion of the cloud of electrons of the oxygen atom transfers to the hydrogen bond [39]. The shift of the $\nu_{\text{O-H}}$ stretching vibration suggests the

existence of hydrogen bond between proline and glycerol when the DES is formed.

Optimization of HPLC chromatographic conditions

The optimization of the analytical conditions was carried out with respect to UV detection wavelength, mobile phase composition and pH. The optimum analytical detection wavelength was carried out at 270 nm, since the maximum absorbance of CA, TH, and IM were observed at 270 nm. The methanol–water and acetonitrile–water mobile phases were investigated in the optimization stage of mobile phase condition. Compared with acetonitrile–water, the chromatogram of the analytes in the methanol–water mobile phase system has less background interference and better resolution. In addition, a small amount of acid was added to the aqueous phase in order to adjust the pH of the mobile phase system. The results showed that the addition of 0.05% phosphoric acid could significantly improve the chromatographic behavior. Figure 3 showed the chromatogram of the mixed standard solution under optimal chromatographic conditions.

Selection of extraction solvent

DES screening is crucial for extracting of the target pesticides from sample matrix due to the following effects:

Figure 2. IR spectra of proline (A); glycerol (B); glycerol-proline (9:4) (C)

Figure 3. Chromatogram of mixed standards of CA, IM, and TH (red); Blank solvent (blue)

diffusion, solubility, viscosity, surface tension, polarity, and physicochemical interactions on solid–liquid extraction. A number of HBAs and HBDs were combined at various ratios according to Section 1.3.1. The selected DESs must meet the following requirements: moderate viscosity for mixing with the sample matrix, higher extraction efficiency for selected analytes, no interference occurred and good chromatographic behavior. Based on the pre-experimental results, we have excluded DESs of ChOx and ChUr and screened out the appropriate DESs for extraction of three pesticides from the sample matrix. As can be seen in the Fig. 4, each DES showed different extraction efficiency for the target compounds. GP-5 exhibited the highest analytical signals among the tested solvents. Therefore GP-5 was selected for the subsequent experiments.

Optimization of extraction solvent volume and extraction time

The optimal volume of the extraction solvent as an important parameter was analyzed. In general, while ensuring the maximum possible amount of the analytes, it should also ensure that the volume of the obtained extracts was sufficient for the further chromatographic analysis. To this purpose, 0.5 g of samples adding a known amount of standard pesticides materials (low concentration in 2.7) was extracted in different volumes of 2 and 4 mL, respectively. The results showed that there was no significant difference in the volume of two selected solvent. Therefore, in the principle of saving energy, we have chosen a small extraction solvent volume of 2 mL as much as possible without affecting the experimental results.

The extraction process was assisted by ultrasound, which can provide the appropriate energy to increase the interaction between the analytes in the matrix and the extraction solution. The analytes can be quickly transferred from the solid phase to the extraction phase in minutes and higher extraction efficiency can be achieved with ultrasound-assisted extraction, so the effect of the extraction time was checked in the range of 10~30 min. The extraction efficiency

stabilized when the extraction time was longer than 20 min. Therefore, 20 min was selected as the extraction time for the further studies.

Optimization of extraction solvent pH

The pH of the sample solution played a significant role in LLE as it determines the existing state of analytes. Optimal pH conditions for LLE were evaluated at the pH of 7 and 9. CA is susceptible to hydrolyzed under acidic condition. When the pH of the aqueous solution is greater than 7, CA is easily extracted into organic solvents due to the low solubility of CA in strong alkaline conditions. However, TH can degrade in higher pH. Moreover, in the selection of pH, some impurities can be transferred from the matrix to the dichloromethane in alkaline conditions, and the impurities can interfere with the target peak in the chromatographic analysis, which affect the quantitative analysis of the target analytes. This indicated that a higher pH value was not a good choice for improving extraction efficiency. Therefore, no change was made to adjust the pH at the end.

Optimization of LLE conditions

The fruit sample matrix contains a large amount of pigment, pectin, cellulose, and polysaccharide components, so the LLE method was used for purification in this study. Petroleum ether is an excellent solvent to remove pigments and less polar impurities from the matrix. Then the analytes was re-extracted with a small amount of dichloromethane. In our work, dichloromethane layer and DES layer extracted by dichloromethane were prepared by drying and dissolving with methanol, and then injected into the instrument for analysis. The results showed that the three pesticides of CA, TH, and IM were successfully extracted into the dichloromethane layer without interference in chromatographic analysis (Fig. 5). The fruit and vegetable sample matrix were purified by the above method, and the recoveries of the analytes were all greater than 85% under the selected chromatographic conditions. It has been verified that the LLE method using petroleum ether and dichloromethane was effective.

Figure 4. Comparison of extraction efficiency of different DESs

Figure 5. Chromatogram of dichloromethane layer (blue); DES layer extracted by dichloromethane (red)

Table 2. Results of linearity, LOQ, LOD for the three analytes

Analytes	Range ($\mu\text{g}\cdot\text{mL}^{-1}$)	Linearity equation	r^2	LOD ($\mu\text{g}\cdot\text{mL}^{-1}$)	LOQ ($\mu\text{g}\cdot\text{mL}^{-1}$)
CA	0.1–10	$y = 38.69x - 4.113$	0.9990	0.05	0.1
TH	0.5–10	$y = 36.91x - 17.70$	0.9993	0.20	0.5
IM	0.1–10	$y = 55.25x - 6.416$	0.9995	0.05	0.1

Table 3. Results of recovery for the three analytes

Analytes	Concentration	Spiked ($\mu\text{g}\cdot\text{mL}^{-1}$)	Average found ($\mu\text{g}\cdot\text{mL}^{-1}$)	Average recovery (%)
CA	Low	1.38	1.49	108.0
	High	6.98	5.98	85.7
TH	Low	2.22	1.92	86.6
	High	6.98	6.39	91.6
IM	Low	1.38	1.56	113.0
	High	6.98	7.60	108.9

Method validation

The analytical performance of the presented method was studied by evaluation of the limits of detection (LODs), limits of quantification (LOQs), linearity and accuracy. The LODs and LOQs were determined as the concentrations with signal-to-noise ratios (S/N) of 3 and 10, respectively. The LODs and LOQs of the method varied from 0.05 to $0.2 \mu\text{g}\cdot\text{mL}^{-1}$ and $0.1\text{--}0.5 \mu\text{g}\cdot\text{mL}^{-1}$, respectively. The linearity of the method was obtained over the range of $0.1\text{--}10 \mu\text{g}\cdot\text{mL}^{-1}$ for CA and IM, $0.5\text{--}10 \mu\text{g}\cdot\text{mL}^{-1}$ for TH, respectively. And the correlation coefficients (r) were greater than 0.9996 for all analytes. The accuracy was determined by adding a known amount of standard pesticides materials to the sample. It was estimated at two concentration levels (low concentration and high concentration). The recoveries of the three targets varied between 85.7 and 113.0%, the relative standard deviations (RSDs) less than 5%, which indicated that the proposed method was stable and reliable. The results were summarized in Table 2 and Table 3.

Real sample analysis

According to current standards GB 2763-2016, the maximum residue limit range of CA, TH, and IM is 3.0–5.0 mg/kg, 3.0–5.0 mg/kg, and 0.5–1.0 mg/kg in above fruit and vegetable samples. The developed method in the extraction and preconcentration of the selected analytes was applied in the analysis of some fruit and vegetable samples. All of the samples were prepared under the optimal extraction conditions and determined under suitable HPLC conditions. The results showed that these samples do not interfere with the determination of the analyte and none of the three target pesticides were detected in real samples.

CONCLUSION

In the present study, a UA-DES-E method combined with LLE was developed for extracting, preconcentration and

determination of three pesticides of CA, TH, and IM from fruit and vegetable matrix. The results proved that DES is an ideal solvent for the extraction of pesticides. A suitable extraction condition was optimized. After optimization, GP-5 (glycerol-proline = 9:4) possessed higher extraction efficiency. The present results highlight that the potential of DES can be utilized for the extraction of micro amount of pesticides in food samples, and no interference is observed from these samples. It provides a new research direction for the use of natural DESs to extract pesticides.

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