Sustainable Chemistry and Pharmacy 30 (2022) 100861

Contents lists available at ScienceDirect

Sustainable Chemistry and Pharmacy

journal homepage: www.elsevier.com/locate/scp

Application of levulinic acid-based natural deep eutectic solvents for extraction and determination of deltamethrin in food samples

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ARTICLE INFO

Keywords:
Levulinic acid
Natural deep eutectic solvent
UV/Vis spectrophotometry
Deltamethrin
Food analysis

ABSTRACT

In the study, a fast and green natural deep eutectic solvent based ultrasound-assisted liquid liquid microextraction (NDES-UALLME) were proposed for the determination and extraction of deltamethrin in food samples using UV/Vis spectrophotometry. The extraction step was based on ion-pair formation between deltamethrin and levulinic acid-tetraethylammonium bromide (as extraction solvent) at pH 5.5, and then extraction of deltamethrin into micro-drops of extraction solvent by using tetrahydrofuran. Levulinic acid-based natural deep eutectic solvents composed of natural, green compounds, *i.e.,* choline acetyl chloride, tetrabutylammonium bromide, tetraethylammonium chloride and tetraethylammonium bromide were used for the first time as extraction solvents for extraction of deltamethrin. The NDES-UALLME procedure allowed to exclude matrixes effects and increase enrichment factor (283) of deltamethrin. Several key factors, including the type and the volume of extraction solvent, the pH of sample solution, ultrasound time, extraction temperature, ionic strength and sample volume were optimized in detail. At optimized conditions, the NDES-UALLME procedure was characterized by low limit of detection (2.4 ng mL^{-1}), a wide linear dynamic range (8–950 ng mL^{-1}), quantitative recoveries (93 ± 4%-103 ± 2%) and acceptable relative standard deviations (2.9%≤). The validation of NDES-UALLME procedure was carried out using recovery tests, intraday and intraday studies. The applicability of NDES-UALLME procedure was confirmed by the assay of deltamethrin in real food samples.

1. Introduction

In plant production, many problems (such as excessive or insufficient irrigation, excessive or insufficient fertilization, weeds, plant pests) are encountered that adversely affect the growth, development and yield of the plant. Plant pests are one of the most important factors that negatively affect the yield and quality of the plant (Hu and Wiatrak, 2012). In plant production, chemical applications are preferred so that plant pests do not cause negative effects on yield and quality, especially in plants with high economic value (El-Hack et al., 2018). The use of chemical applications in the control of plants against diseases, pests and weeds is over 95% compared to other agricultural control methods (Hu and Wiatrak, 2012). Pesticides, which are frequently applied chemicals in agricultural production areas, are used to protect the productivity of the plant (Parween et al., 2016).

Pesticides are substances that prevent the transmission of harmful organisms to the plant or provide the protection of the plant. According to the areas of use of pesticides, algicide (fighting algae), avicide (fighting birds), bactericide (fighting bacteria), fungicide (fighting fungi), herbicide (combating weeds), insecticide (fighting insects), acaricide (mites), molluscicide (fighting slugs and

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https://doi.org/10.1016/j.scp.2022.100861
Received 25 June 2022; Received in revised form 10 September 2022; Accepted 24 September 2022
Available online 13 October 2022

snails), nematicide (fighting nematodes), rodenticide (controlling rodents) and virucidal (controlling viruses) (EPA, 2009). The products used for the protection of plants in agricultural production in the world contain chemicals including 48% herbicides, 30% insecticides, 18% fungicides and 7% nematicides (Kang et al., 2016). Long-term applications of pesticides have negative effects on both the environment and human health (Liu et al., 2019). The pesticide residues used are in the soil, water, and animal or vegetable products; it causes negative effects on non-target organisms, environmental pollution and resistance development in pests (Kamal et al., 2020). Therefore, consuming agricultural products with pesticide residues will cause health problems (Fantke et al., 2013). Insecticides are chemicals used to combat harmful insects in agricultural areas. Insecticides are used in almost every field, but they harm the environment from beneficial soil microorganisms to insects, fish and birds (Mulé et al., 2017). In recent years, studies have been increasing to obtain safer options against chemical insecticides in order to control possible insect damage on plants (Amoabeng et al., 2019).

UV–vis spectrophotometer is widely used for the determination of organic/inorganic species due to its simplicity, cheapness, rapid measurement and availability in almost every research laboratory (Doğan et al., 2020). The biggest problem in this determination technique is that the analyte concentration to be determined is too low and the determination cannot be made correctly due to interferences originating from the matrix environment (Mello et al., 2013). Separation/preconcentration methods such as liquid-liquid, solid-liquid and solid phase extraction are widely used to prevent interference and bring the analyte concentration above the detection limit (Fisher and Kara, 2016). These methods are the ones that take a long time, involve complex extraction steps, and are desired to use large amounts of sample and solvent (Fisher and Kara, 2016). Due to such disadvantages, interest in microextraction methods that minimize organic solvent consumption, allow automation, simplify extraction steps and provide better enrichment factor has recently increased (Soares da Silva Burato et al., 2020). In these methods, since the extraction solvent at the microliter level is used, direct analyzes of the analytes can be made without the need for any evaporation process (Sajid and Płotka-Wasylka, 2018). High extraction yields and enrichment factors can be obtained for analytes in microextraction methods. In addition, very low levels of analytes can be detected sensitively.

The effectiveness of an extraction solvent depends on its dissolution properties. natural deep eutectic solvents (NDES) has the ability to donate and accept protons and electrons, giving them the ability to form hydrogen bonds, thus increasing their dissolving capacity. The reason for the increase in scientific publications, especially in extraction studies, can be attributed to the unique properties of these new liquids such as high thermal stability, low thermal conductivity, low volatility and tunable miscibility, as well as their ability to be combined with many spectroscopic techniques. (Soltanmohammadi et al., 2021).Moreover, as NADES are greener and safer alternatives, it is not surprising that they have also been used in the extraction of real samples for food, environmental and pharmaceutical applications. NADES has good properties to be used as alternative extraction solvents such as being liquid at room temperature, easily adjustable in viscosity, sustainable and safe. (Taşpınar et al., 2021; El Achkar et al., 2021; Paiva et al., 2014). The use of NDES as extraction solvents has many advantages over conventional solvents. First of all, since their polarity is quite high, NDESs have the ability to dissolve many organic or inorganic substances, such as cellulose, which are insoluble in conventional solvents (El Achkar et al., 2021). In addition, NDESs are described as environmentally friendly solvents. The NDEs; It consists of organic substances and is inexpensive, biodegradable, non-flammable, non-volatile, environmentally friendly (non-toxic), easy to prepare, odorless and colorless solvents (Santana-Mayor et al., 2021). The NDESs are solvents with high viscosity and low ionic conductivity. The NDESs have attracted attention in recent years due to these advantages mentioned above.

The purpose of this research was to propose a simple and green microextraction procedure for the extraction and preconcentration of deltamethrin in food samples by natural deep eutectic solvent ultrasound-assisted liquid-liquid microextraction (NDES-UALLME) prior to its quantification by UV/Vis spectrophotometry. The effect of important microextraction parameters were optimized in detail. The precision and accuracy of the method was tested with intraday and interday studies. . The most important innovation of the study is the testing of levulinic acid-based NDESs for the extraction of deltamethrin, because, to the best of our knowledge this is the first report of using NDES-UALLME procedure to extract deltamethrin in food samples for spectrophotometry. In addition, the findings showed that the relevant NDESs can be successfully applied to the extraction of deltamethrin. Application results have shown that the NDES-UALLME procedure was not only simple and green, but also highly efficient and reproducible without the need for special equipment.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade. Deltamethrin (purity >98%), levulinic acid (4-Oxopentanoic acid, purity >98%), choline acetyl chloride (CAC, purity >99%), and tetrabutylammonium bromide (TBAB, purity >98%) were supplied from Sigma-Aldrich (USA). Tetraethylammonium chloride (TEAC, purity >98%) and tetraethylammonium bromide (TEAB, purity >98%) were supplied from Merck (Darmstadt, Germany). Stock solution of deltamethrin (100 mg L^{-1}) was prepared by dissolving the appropriate amount of its solid in acetone. Working solutions and calibration solutions were obtained by daily sequential dilution of the stock solution. Acetate buffer solution (0.1 M pH = 5.5) was prepared by dissolving appropriate amounts of sodium acetate and glacial acetic acid in ultrapure water.

2.2. Apparatus

The determination step was performed on a UV–Visible Spectrophotometer (Shimadzu UV-1800 PC model, Tokyo, Japan). Ultrasonic bath (A SK5210LHC Kudos, Shanghai, China), digital pH-meter (Mettler Toledo FE28, Zurich, Switzerland), rotary evaporator (BUCHI R-200, Labortechnik AG, Flawil, Switzerland) and centrifuge (Universal-320, Hettich, London, England) were used in the extraction step. Ultra-pure water obtained from Milli-Q water purification system (Millipore, USA) was used for all studies.

2.3. Sampling and sample preparation

The study was carried out in 3 replications under greenhouse conditions in plastic pots with a capacity of 3 kg at Sivas Cumhuriyet University. The soil used in the study was taken from a depth of 0–20 cm from the university research trial area and passed through a 2 mm sieve, and some soil properties are given in Table 1. Accordingly, the soil is slightly alkaline, unsalted, calcareous, and has a low organic matter content. In the study, tomato, pepper, eggplant, wheat, maize, barley and chickpea plants were used as test plants. Initially, for chickpea 100 mg N kg^{-1}, for other pants 150 mg N kg^{-1}, for all plants 100 mg P kg^{-1} and 125 mg K kg^{-1} were applied to each pot as basic fertilization (in the form of $CaNO_3.4H_2O$, KH_2PO_4, respectively). After the plants germinated, weed insecticide application containing 25 g L^{-1} Deltamethrin was applied 3 times at one week intervals. In addition, a control group that did not apply any herbicide to the same plants was formed. The plants were harvested approximately 55 days after planting.

In the study, the extraction process was done by Kenari et al. (2014) used in their studies according to the proposed method. For this, the harvested tomato, pepper, eggplant, wheat, maize, barley and chickpea plants were dried at room temperature and in the shade. Dry plant materials were ground into powder in a laboratory type grinder. Afterwards, distilled water (dH_2O) was added as a solvent at a ratio of 10:1 on the powdered plant materials. It was left to macerate on a shaker at 150 rpm for 24 h. It was filtered with a Whatman No. 1 filter paper and the solvent (dH_2O) was evaporated in a rotary evaporator at 40 °C.

2.4. NADESs preparation

In the current study, four different NDESs such as levulinic acid (LA)-choline acetyl chloride (CAC), LA-Tetraethylammonium chloride (TEAC), LA-tetrabutylammonium bromide (TBAB) and LA-tetraethylammonium bromide (TEAB) were prepared and tested for the extraction of deltamethrin. The relevant NDESs were prepared according to the previously reported study (Li et al., 2016). These NADESs were prepared by heating different two-component mixtures to 80 °C with constant stirring and under atmospheric pressure until a homogeneous phase. Finally, the resulting NDESs were dried under vacuum at 353 K for 48 h before the studies.

2.5. NDES-UALLME procedure

In brief, 850 μL of NADES-3 (LA-TEAB at 1:3 M ratio) was poured into a 15-mL conical tube containing 10 mL sample solution or standard solution with pH equal to 5.5 adjusted by the addition of 0.1 mol L^{-1} acetate buffer solution. The resulting mixture was then sonicated in an ultrasonic bath at 40 °C for 8 min to disperse the extraction solvent and improve the diffusion coefficients. At this stage, the resulting mixture looked cloudy because the NADES-3 (extraction solvent) formed microspheres. In order to accelerate the separation of the DES solvent from the aqueous phase as the top layer, 400 μL of tetrahydrofuran was quickly added to the resulting mixture using a microsyringe. Afterwards, the mixture was centrifuged at 4000 rpm for 2 min. The NDES layer was clearly separated above the aqueous phases. The upper NDES layer (approximately 200 μL) was subjected to UV/Vis spectrophotometry (562 nm). All studies were carried out in triplicate.

2.6. Calculation of extraction recovery

Extraction recovery (ER%) was used to indicate the best value of the optimized factors. The ER% was calculated using the following equation-1:

$$ER\% = \times 100\ [C_{measured}\text{-}C_{real}]/C_{spiked} \quad (1)$$

Where $C_{measured}$, C_{real}, and C_{spiked} were the detected amount of deltamethrin in sample solution after adding a certain amount of the standard deltamethrin solution, the amount of deltamethrin in sample solution without addition of standard deltamethrin solution, and the amount of standard deltamethrin solution spiked into the sample solution, respectively.

Table 1
Some physical and chemical properties of the soils used in the study.

Soil Property	Depth (0–20 cm)
pH	7.84
Lime (%)	17.1
Salt (%)	0.021
Organic matter (%)	1.68
Texture	SiCL
Total N (%)	0.087
Available P (kg ha^{-1})	44.3
Available K (kg ha^{-1})	992.4
Available Fe (mg kg^{-1})	3.11
Available Mn (mg kg^{-1})	2.02
Available Zn (mg kg^{-1})	0.47
Available Cu (mg kg^{-1})	1.37

3. Results and discussion

3.1. Optimization of the NDES-UALLME procedure

The extraction step was based on ion-pair formation between deltamethrin and levulinic acid-tetraethylammonium bromide (as extraction solvent) at pH 5.5, and then extraction of deltamethrin into micro-drops of extraction solvent by using tetrahydrofuran. So, key factors of the NDES-UALLME procedure including the selection of suitable NDES, molar ratio of selected NDES, volume of selected NDES, pH of sample solution, ultrasound time, extraction temperature, ionic strength and sample solution were optimized in detailed.

3.1.1. Selection of suitable NDES as extraction solvent

The main parameter to be optimized is the selection of the appropriate extraction solvent. The extraction solvent should efficiently, rapidly and selectively extract the target analyte from the sample solution. Furthermore, extraction solvents are desired to be environmentally friendly due to the toxic properties of organic solvents. NDES prepared from the interaction of levulinic acid with different HBA groups exhibit different physicochemical properties. Their effectiveness for deltamethrin may differ. Therefore, the most suitable choice of DES was investigated for the extraction of deltamethrin using different NDESs equimolar. The composition of these prepared NADES, their molar ratios and the ER% obtained as a result of the application are presented in Table 2. In this study, all NADES prepared were used in a molar ratio of 1:2. From the results, the order of ER% for deltamethrin was NADES-3 (LA-TEAB, 91.7%) > NADES-1 (LA-CAC, 83.6%) > NADES-4 (LA-TEAC, 71.8%) > NADES-2 (LA-TBAB, 70.1%), respectively. Also, the high viscosity of NADES-1, 2 and 4 makes it difficult to separate the two phases after extraction step. Based on the results obtained, NADES-3 prepared from a mixture of LA and TEAB was chosen as the suitable extraction solvent.

3.1.2. Influence of molar ratio of NDES-3

The effectiveness of NADES in extraction studies depends on the molar ratio of its constituent components. Therefore, appropriate molar ratios of the main components of NADES should be investigated to ensure efficient and easy phase separation of the target analyte using NADES. Because NADES provides with H-bond, the effectiveness of this bond depends on the molar ratio of the components in the aqueous solution. In the light of these explanations, different molar ratios of LA and TEAB bromide forming NDES-3 were mixed and tested for the extraction of deltamethrin. The results in Fig. 1 showed that the ER% of deltamethrin increased rapidly as the molar ratio increased from 2:1 to 1:3, and then remained constant, which clearly showed that the NADES extraction capacity was affected by the molar ratio of components. The probable reason for this may be that hydrogen bonding occurs more easily and effectively by increasing the electron exchange depending on the increasing amount of TEAB in the composition. As a result, the appropriate molar ratio of NADES-3 was chosen as 1:3 for further studies.

Table 2
List of the prepared levulinic acid-based natural deep eutectic solvents for extraction of deltamethrin.

Symbol	Abbreviation	Component-1 (HBD)	Component-2 (HBA)	Molar ratio	ER (%)
NADES-1	LA-CAC	levulinic acid	choline acetyl chloride	1:2	83.6
NADES-2	LA-TBAB	levulinic acid	tetrabutylammonium bromide	1:2	70.1
NADES-3	LA-TEAB	levulinic acid	tetraethylammonium bromide	1:2	91.7
NADES-4	LA-TEAC	levulinic acid	tetraethylammonium chloride	1:2	71.8

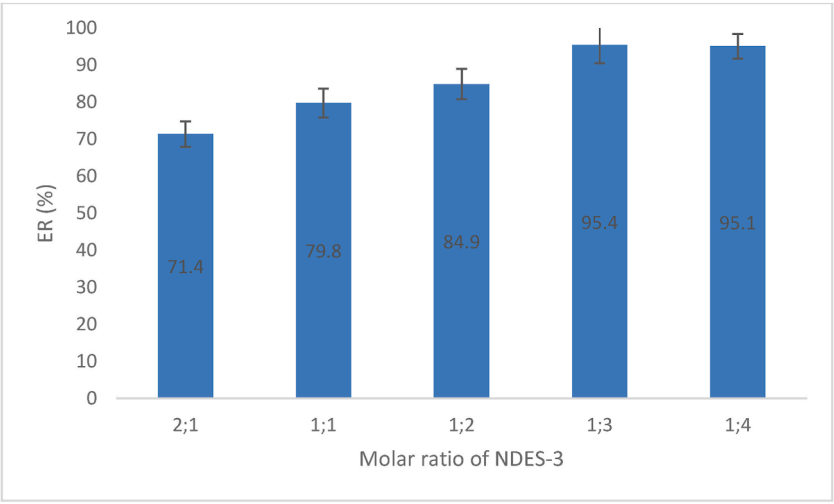

Fig. 1. Effect of molar ratio of NDES-3 on the ER% of deltamethrin.

3.1.3. Influence of volume of NDES-3

In extraction studies, it is necessary to add sufficient amount of extraction solvent to the sample solution in order to extract the target analyte from the sample solution effectively and quantitatively. Therefore, the volume of the extraction solvent is a very important parameter that directly affects the extraction recovery by enriching or diluting the analyte concentration. On the one hand, insufficient extraction solvent can lead to insufficient extraction. On the other hand, excess volume of extraction solvent will reduce extraction efficiency due to dilutionand accordingly, the enrichment factor decreases. For these reasons, the effect of volume of NADES-3 on the ER% of deltamethrin was tested in the range of 100–1200 μL. The results in Fig. 2 show that the ER% of deltamethrin increases as the volume of NDES-3 increases up to 850 μL, and there is a drastic decrease after this volume. As a result, the appropriate volume of NADES-3 was chosen as 850 μL for further studies.

3.1.4. Influence of pH of sample solution

The pH of the sample solution is very important in studies such as extraction where interaction between chemical species is important. Because, the pH value of the solutions will change the degree of ionization and speciation of the analytes, as well as affect the partition coefficient and extraction efficiency of the target compounds (Qiao et al., 2021) accordingly, the interaction of the target analyte with the extraction solvent may increase or decrease. For these reasons, pH is an important parameter that needs to be optimized in extraction studies in aqueous solutions. Based on the explanations, the effect of the pH of the sample solution on the ER% of deltamethrin was tested in the pH range of 2.5–10.5 using different buffer solutions. The results in Fig. 3 showed that the ER% of deltamethrin peaked at pH 5.5 and then gradually decreased and remained stable after pH 8.5. In the basic regions, the decrease in recovery is probably due to the loss of protons from levulinic acid. As a result, the appropriate value of pH of sample solution was chosen as pH 5.5 for further studies.

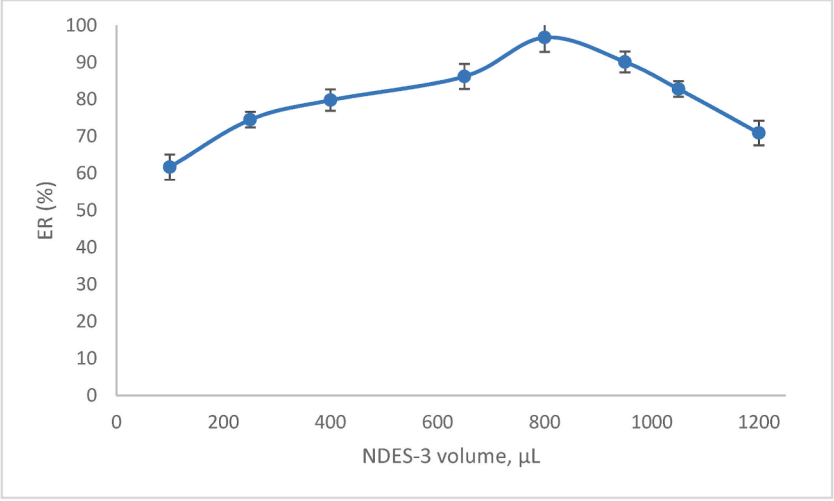

Fig. 2. Effect NDES-3 volume on the ER% of deltamethrin.

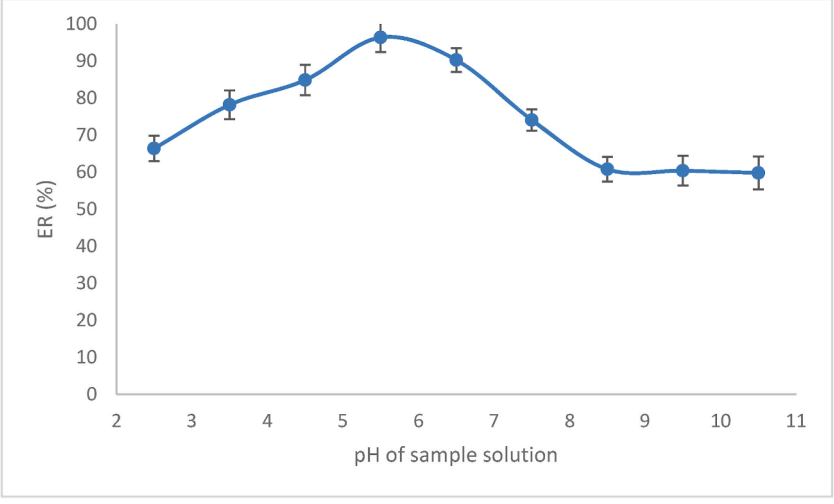

Fig. 3. Effect of pH of sample solution on the ER% of deltamethrin.

3.1.5. Influence of extraction temperature

Generally, in extraction studies using deep eutectic solvent, surfactant and ionic liquid as the extraction solvent, they must form nanosized microspheres in the sample solution in order to achieve phase separation. In order to achieve this, a cloudy appearance should be obtained after the extraction solvent is added to the sample solution. Physical steps such as vortex, ultrasound, heating and salt addition are generally used to achieve this. In this study, a heating step was required because a cloudy appearance could not be obtained at room temperature after NADES-3 was added to the sample solution. In this context, the effect of extraction temperature on the ER% of deltamethrin was tested in the range of 30 °C–65 °C. The results in Fig. 4 showed that the ER% of deltamethrin increased significantly as the extraction temperature increased from 30 °C to 45 °C, remained stable in the 45°C-55 °C extraction temperature range and decreased after 55 °C. As a result, the appropriate value of extraction temperature was chosen as 45 °C for further studies.

3.1.6. Influence of ultrasonication time

Ultrasonication can help disperse the extraction solvent into the sample solution and accelerate the mass transfer of target compounds to achieve equilibrium faster and increase extraction efficiency. Therefore, the effect of ultrasonication time on the ER% of deltamethrin was tested in the range of 1–20 min at 45 °C. The results in Fig. 5 show that 8 min of ultrasonication time is sufficient for quantitative the ER% of deltamethrin. No significant change in the ER% of deltamethrin was observed with ultrasonication applications over 8 min. As a result, the appropriate value of ultrasonication time was chosen as 8 min for further studies.

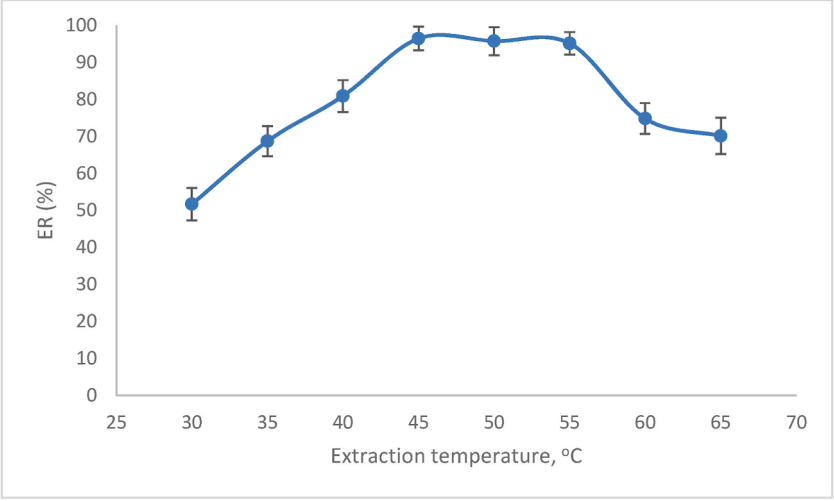

Fig. 4. Effect of extraction temperature on the ER% of deltamethrin.

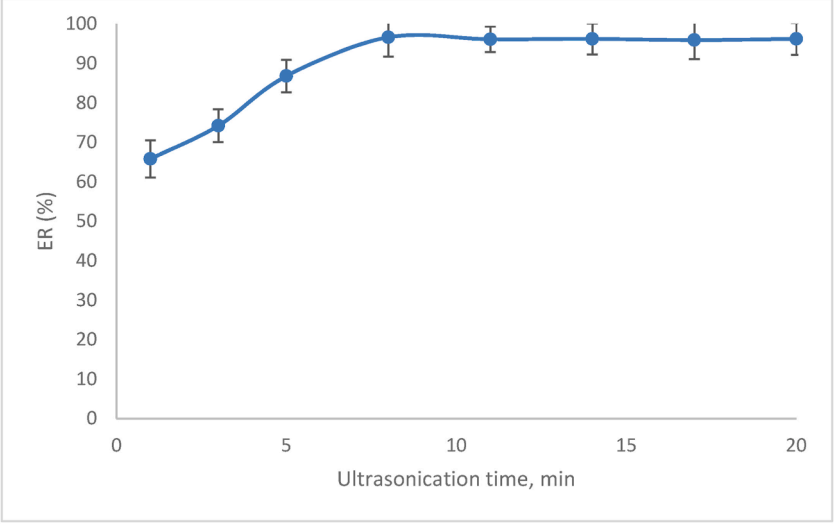

Fig. 5. Effect of ultrasonication time on the ER% of deltamethrin.

3.1.7. Influence of THF volume

THF was used as the aprotic solvent to ensure efficient separation of the NDES-3 in the sample solution. THF has the ability to dissolve a wide variety of polar and non-polar compounds due to its properties such as moderate polarity, low surface tension and low enthalpies of evaporation. THF penetrates the extraction complex more easily than water, thus improving solvent contact with the extraction complex. The most important factor in providing these is the THF volume to be used. Therefore, the effect of THF volume on the ER% of deltamethrin was tested in the range of 50–600 μL. The results in Fig. 6 show that 400 μL of THF is sufficient for quantitative analytical results. As a result, the appropriate value of THF volume was chosen as 400 μL for further studies.

3.2. Method validation and application for analysis of food samples

3.2.1. Determination of analytical parameters of the NDES-UALLME procedure

Analytical parameters of the NDES-UALLME procedure such as linear dynamic range (LDR), regression equation, determination coefficient (r^2), limit of detection (LOD), limit of quantification (LOQ), enrichment factor (EF), extraction recovery (ER) and relative standard deviation (RSD) were determined to exhibit the method performance. LOD (2.4 ng mL^{-1}) LOQ (8 ng mL^{-1}) and EF (283) were calculated using the following equations-2 and 3:

$$LOD = 3s_{blank}/m \quad (2)$$

$$LOQ = 10s_{blank}/m \quad (3)$$

$$EF = C_f/C_i \quad (4)$$

Where s_{blank} was the standard deviation of the sample blank, b was the slope of the calibration curve. C_f was the final concentration of deltamethrin, C_i was the initial concentration of deltamethrin, respectively. Moreover, linear dynamic range was 8–950 ng mL^{-1} with the r^2 value of 0.9969. Following studies for 50 and 250 ng mL^{-1} of deltamethrin, RSD and extraction recovery were in the range of 1.3–2.4% and 94.4–97.9%, respectively. Detailed results were given in Table 3.

3.2.2. Interference studies

To evaluate the selectivity of the NDES-UALLME procedure, the interference from matrix ions commonly found with deltamethrin were investigated by adding a known concentration of matrix ions and some pesticides to 10 mL sample solution including 20 μg of deltamethrin. Afterwards, the obtained mixture was analyzed by the NDES-UALLME procedure. As a result of this study, the tolerable limit was determined for each matrix ion and pesticide. The tolerance limit of the matrix ions does not cause a deviation of more that ±5% in absorbance of deltamethrin. In addition, analytical results including RSD and recovery for the studied species are presented in Table 4. The high tolerable limit, low RSD and quantitative recovery results in Table 4 show that the NDES-UALLME procedure exhibits good selectivity for deltamethrin.

3.2.3. Intra/inter-day studies for accuracy and precision

The accuracy and precision of the method were investigated by calculating recovery and RSD, respectively. In this context, accuracy and precision were determined in terms of the intra-day and inter-day using 100, 400 and 800 ng mL^{-1} levels for deltamethrin in working solutions. For these concentrations, three repetitive studies were performed on the same day in the intraday study, and three repetitions were performed on three consecutive days in the interday study. Intraday RSD and Inter-day RSD were in the range of

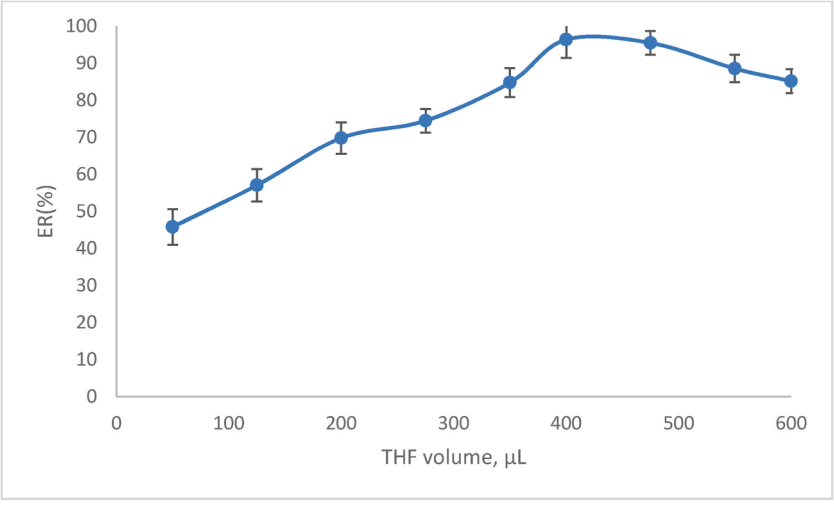

Fig. 6. Effect of THFvolume on the ER% of deltamethrin.

Table 3
Analytical performance of the NDES-UALLME procedure.

Analytical parameters	After NDES-UALLME procedure	Before NDES-UALLME procedure
Regression equation $A = (a \pm SD_a)\ c + (b \pm SD_b)$	$A = (0.6217 \pm 0.0238)C + (0.3369 \pm 0.0452)$	$A = (0.0095 \pm 0.0003)C + (0.0236 \pm 0.0017)$
r^2	0.9969	0.9978
LDR, ng mL^{-1}	8–950	500–6000
LOD, ng mL^{-1}	2.4	152
LOQ, ng mL^{-1}	8	500
RSD	1.3–2.4	–
ER	94.4–97.9	–
EF	283	–

A, absorbance of deltamethrin; c, deltamethrin concentration in food samples (ng mL^{-1}); a, slope; b, intercept; SD_a and SD_b, standard deviations of slope and intercept, respectively.
LDR: Linear dynamic range.
r^2: Determination coefficient.
LOD: Limit of detection.
LOQ: Limit of quantification.
RSD: Relative standard deviation for 50 and 250 ng mL^{-1} of deltamethrin.
ER: Extraction recovery for 50 and 250 ng mL^{-1} of deltamethrin.
EF: enrichment factor.

Table 4
Selectivity study for deltamethrin of the NDES-UALLME procedure (N = 3).

Matrix ions	Tolerable limit	RSD (%)	Recovery (%)
K^+	2000	1.4	99 ± 3
Na^{2+}	2000	1.8	99 ± 2
Mg^{2+}	2000	1.5	97 ± 4
Fe^{2+}	2000	1.3	98 ± 3
Mn^{2+}	1500	1.8	99 ± 3
Zn^{2+}	1500	1.6	97 ± 4
Cu^{2+}	1500	1.8	97 ± 2
Permethrin	1000	2.0	96 ± 2
Pyriproxyfen	750	1.9	98 ± 4
Progesterone	750	2.2	97 ± 4
Cyhalothrin	750	2.1	97 ± 3
Cypermethrin	500	2.3	96 ± 3
Flumethrin	500	1.9	95 ± 4
Tralomethrin	250	2.3	95 ± 3

1.4–2.0% and 1.7–2.3%, respectively. In addition, intraday recovery and Inter-day recovery were in the range of 94.7–98.3% and 92.2–96.8%, respectively. The obtained results showed that the NDES-UALLME procedure exhibits good accuracy and precision.

3.2.4. Analysis of food samples

The applicability of the NDES-UALLME procedure in the analysis of trace amounts of deltamethrin was investigated by analyzing some food samples such as tomato, pepper, eggplant, wheat, maize, barley and chickpea. Table 5 shows analytical value of standard solution (at amounts of 200 and 400 ng mL^{-1} of deltamethrin), added the selected food samples (at amounts of 200 and 400 ng mL^{-1} of deltamethrin), and the selected food samples without added. Added and without added food samples were analyzed after the NDES-UALLME procedure was applied to them, while the standard solution was injected directly. Relative recoveries of deltamethrin were calculated by multiplying by 100 the ratio between the concentration found in each sample and the concentration found in deionized water added at the same level. The analytical results in Table 5 indicate the good recoveries (93 ± 4%-103 ± 2%) and acceptable relative standard deviations (2.9%≤), thus demonstrating its usefulness for extraction and determination of low amounts of deltamethrin in food samples.

3.3. Comparison with other analytical methods

The significant analytical parameters of the NDES-UALLME procedure (LDR, LOD, EF, ER, RSD and extraction time) were compared with other analytical methods. The results were summarized in Table 6. The LOD of our NDES-UALLME procedure was found to have a wider range than the analytical methods reported. The obtained LOD and ER values were satisfactory and comparable to the methods mentioned. The precision of the method was satisfactory and the RSD values were comparable to those of the analytical methods reported. The EF was better than the mentioned methods and the extraction time of our method was is shorter than all analytical methods. In addition, the extraction solvents used in this study were quite easy to prepare. In addition, expensive reagents and toxic organic solvents were not used.

Table 5
Determination and extraction of deltamethrin in food samples using NDES-UALLME procedure (N = 3).

Food samples	Spiked (ng mL^{-1})	Intra-day			Inter-day		
		Found ± SD[a] (ng mL^{-1})	Recovery ± SD[a] (%)	RSD (%)	Found ± SD[a] (ng mL^{-1})	Recovery ± SD[a] (%)	RSD (%)
Tomato	200	194 ± 8	97 ± 3	1.3	192 ± 11	96 ± 4	1.7
	400	396 ± 19	99 ± 2	1.6	392 ± 20	98 ± 3	1.9
Pepper	200	190 ± 7	95 ± 3	1.9	188 ± 9	94 ± 5	2.2
	400	392 ± 18	98 ± 4	2.2	388 ± 20	97 ± 3	2.5
Eggplant	200	190 ± 9	95 ± 3	1.8	186 ± 10	93 ± 4	2.1
	400	388 ± 17	97 ± 3	2.1	380 ± 19	95 ± 3	2.4
Wheat	200	194 ± 8	97 ± 4	2.1	206 ± 12	103 ± 2	2.6
	400	396 ± 20	99 ± 3	2.5	408 ± 23	102 ± 1	2.9
Maize	200	192 ± 9	96 ± 3	1.6	188 ± 10	94 ± 3	2.0
	400	392 ± 19	98 ± 2	1.8	384 ± 19	96 ± 3	2.3
Barley	200	196 ± 9	98 ± 2	2.1	190 ± 9	95 ± 2	2.5
	400	396 ± 18	99 ± 3	2.4	388 ± 19	97 ± 2	2.7
Chickpea	200	204 ± 10	102 ± 3	2.2	206 ± 11	103 ± 2	2.6
	400	404 ± 20	101 ± 2	2.5	404 ± 22	101 ± 2	2.8

[a] Standard deviation (n = 4, 95% confidence interval).

Table 6
Comparison of the NDES-UALLME procedure with other methods used in extraction and determination of the deltamethrin.

Analytical methods	LDR (ng mL^{-1})	LOD (ng mL^{-1})	EF	ER (%)	RSD (%)	Extraction time (min)	References
HLLME-FA-GC-FID	1–200	0.2	–	90–98	≤6.9	60	Haddadi et al. (2014)
USA-MNF-LPME-GC-MS	1–250	2.68	415.8	91–101.8	≤3.2	15	Shirani et al. (2019)
MAE-UADLLME-HPLC	55–3560	11.6	63.8	83.7–87.7	≤5.6	4	Wang et al. (2018)
ETA-SPS-HLPME-GC-FID	0.5–2500	0.16	194	93–97	≤4.93	8	(Asadi et al., 2022)
MSPE-DLLME GC-FID	0.5–100	0.1	–	80–95	≤4.0	20	Noori et al. (2017)
NDES-UA-LLME- UV/Vis spectrophotometry	8–950	2.4	283	94.4–97.9	1.3–2.4	8	Current study

LDR: Linear dynamic range.
LOD: Limit of detection.
LOQ: Limit of quantification.
RSD: Relative standard deviation.
ER: Extraction recovery.
EF: Enrichment factor.
HLLME-FA-GC-FID: Homogeneous liquid–liquid microextraction via flotation assistance gas chromatography - flame ionization detector.
ETA-SPS-HLPME: Effervescent tablet-assisted switchable polarity solvent–based homogeneous liquid-phase microextraction gas chromatography–flame ionization detection.
MAE-UADLLME-HPLC: Microwave-assisted extraction and ultrasonic-assisted dispersive liquid-liquid microextraction high performance liquid chromatography.
NDES-UA-LLME- Natural deep eutectic solvent ultrasound-assisted liquid liquid microextraction.
MSPE-DLLME GC-FID: Magnetic solid phase extraction coupled with dispersive liquid-liquid microextracton gas chromatography-flame ionization detector.
USA-MNF-LPME-GC-MS: ultrasound assisted magnetic nanofluid based liquid phase microextraction gas chromatography-mass spectrometry.

4. Conclusions

The paper presents a simple, fast and green analytical procedure based on the use of a natural deep eutectic solvent ultrasound-assisted liquid liquid microextraction for the determination and extraction of deltamethrin in food samples using UV/Vis spectrophotometry. Levulinic acid-based natural deep eutectic solvents composed of natural, green compounds, *i.e.,* choline acetyl chloride, tetrabutylammonium bromide, tetraethylammonium chloride and tetraethylammonium bromide were used for the first time as extraction solvents for extraction of deltamethrin. Key factors of the NDES-UALLME procedure including the selection of suitable NDES, molar ratio of selected NDES, volume of selected NDES, pH of sample solution, ultrasound time, extraction temperature, ionic strength and sample solution were optimized in detailed. Under the optimized condition, a very low LOD value as good 2.4 ng mL^{-1}, a wide LDR of 8–950 ng mL^{-1} (r2 = 0.9969), and a short extraction time equal to 8 min was obtained. The EF was 283 that was quite favorable for an extraction procedure. Finally, the new natural deep eutectic solvents was tested for extraction and determination of deltamethrin in tomato, pepper, eggplant, wheat, maize, barley and chickpea and the RSD and recovery% were obtained in the range of 1.4–2.9% and 93 ± 4%-103 ± 2%, respectively.

Funding

The authors received no financial support for the research, authorship and/or publication of this article.

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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

The authors do not have permission to share data.

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