



Ultrasound-assisted dispersive liquid-liquid microextraction based on solidification of floating organic drop for analysis of propineb in water and food samples: Experimental modeling

Adil Elik^a, Nail Altunay^{a,*}

^a Faculty of Science, Department of Chemistry, Sivas Cumhuriyet University, Sivas, Turkey

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ABSTRACT

Here, a fast and simple ultrasound-assisted dispersive liquid-liquid microextraction based on solidification of floating organic drop using deep eutectic solvent (UA-DLLME-SFO-DES) procedure was optimized for the extraction of propineb from water and food samples prior to analysis by UV-VIS spectrophotometer. In this research, the extraction step was carried out by using DESs as the extraction solvent. The optimization of the significant variables of the UA-DLLME-SFO-DES procedure was carried out by multivariate statistical method. After multivariate optimization, linearity range was observed from 20 to 450 ng mL⁻¹. The detection limit, preconcentration factor, and enhancement factor were estimated as 6.1 ng mL⁻¹, 120, and 93, respectively. The calibration curve of the UA-DLLME-SFO-DES procedure was estimated at $A = 0.0074-0.015$ [propineb, ng mL⁻¹]. Intra- and inter-day precisions were $\leq 1.9\%$ and $\leq 2.8\%$, respectively. Recoveries between 90.4% and 98.6% indicated the absence of matrix effects, indicating that the UA-DLLME-SFO-DES procedure was suitable for the extraction and determination of propineb in water and food samples. The UA-DLLME-SFO-DES procedure was an efficient, simple, and cheap alternative to other extraction and determination techniques, and can be used for routine monitoring of propineb in complex matrices.

1. Introduction

Propineb [Zinc propylenebis (dithiocarbamate)] is widely used as a fungicide in the Mediterranean region. In addition, due to its wide spectrum of action on fungi, its usage area is becoming widespread. (Anastassiadou et al., 2021). The main reason for its widespread use is its high chemical and biological activities and low production cost (Medina-Pastor et al., 2020; Santovito et al., 2012). Studies have reported that long-term exposure to the propineb by mouth or inhalation may cause health problems such as carcinogenicity, teratogenicity, malfunction of the reproductive system, and malformation of vital organs (Kazos et al., 2007; WHO, 1993). Maximum residue level of propineb in food and vegetable samples should be in the range of 0.05–50.0 mg kg⁻¹ (Official Gazette of the Republic of Turkey, 2013). Therefore, it is important to develop new analytical inexpensive method for the rapid, and selective determination of propineb in real samples.

The use of analytical approaches were the primary means of monitoring the amounts of propineb in different samples. Chromatography-based methods, spectroscopic methods, and electroanalytical analytical methods are powerful tools because of their detection capabilities (Montaseri and Forbes, 2018). Gas chromatography with flame photometric detection (GC-FPD) (Song et al., 2018), GC-

* Corresponding author.

E-mail address: naltunay@cumhuriyet.edu.tr (N. Altunay).

mass spectrometry (Bodur et al., 2020), flame atomic absorption spectrometry (Soylak et al., 2022), liquid chromatography-tandem mass spectrometry (Vaclavik et al., 2018) and UV-VIS spectrophotometer (Öter and Zorer, 2022) techniques have been reported for the determination of propineb in different samples. Determination of propineb using these techniques is successful when propineb is extracted with an appropriate sample preparation procedure. The extraction step removes the analytes from the sample solution and increases the analyte concentration (Jouyban et al., 2020). The requirement to perform a sample preparation method prior to instrumental analysis of propineb is more important in samples with complex matrices. Therefore, it is essential to develop an appropriate sample preparation procedure to enrich, extract and determine propineb in food matrices.

Various extraction methods including solid-phase extraction (G. Liu et al., 2018) and liquid-liquid extraction (Wu et al., 2010) have been applied to extract pesticides from different samples. However, these procedures are often time-consuming, generate low enrichment factors, and require large amounts of organic solvents (Lanjwani et al., 2023). Thus, miniaturization of the sample preparation process as microextraction procedures has been developed. Various microextraction procedures such as solid-phase microextraction (Liang et al., 2019), supercritical fluid extraction with dispersive liquid-liquid microextraction (Naeeni et al., 2011), coprecipitation (Soylak et al., 2022), dispersive solid-phase microextraction (Vaclavik et al., 2018), and dispersive liquid-liquid microextraction (Bodur et al., 2020) have been successfully applied for the analysis of propineb in the real samples. These microextraction procedures have shown better results for the analysis of different chemical species in various matrices due to the ease and effectiveness of the methods.

Meanwhile, the preparation and application of green solvents such as ionic liquids (ILs), supramolecular and deep eutectic solvents (DESs) in the microextraction procedures have received much attention (Hashemi et al., 2018). The DESs are a new class of solvents derived from renewable resources, characterized by a remarkable decrease in melting point compared to the starting components (Liu et al., 2022). The DESs can be easily prepared by mixing a hydrogen bond acceptor (HBA) with a hydrogen bond donor (HBD). One of the reasons for giving importance to DESs is that these solvents are low toxicity, non-volatile, non-flammable, and biodegradable liquids (Haq et al., 2022, 2023; Płotka-Wasyłka et al., 2020). Although the toxicity of DESs is quite low, there are studies in the literature reporting the existence of some conditions that should be considered. For example, when examining DES toxicity on some bacteria, it has been reported that the cytotoxicity of some DES species is higher than the individual toxicity of its components (eg. glycerin, choline chloride) (Hayyan et al., 2013). Another reason is the ease of preparation and the large number of possible starting materials that can be used to develop a suitable DES for particular applications (Musarurwa and Tavengwa, 2021). Recently, researchers have taken advantage of the superior properties of DESs in the analysis of real samples, including aflatoxin M1, butylparaben, triclosan, fluoroquinolones, lignans, tert-butylhydroquinone, and anti-prostate cancer triple therapy (El-Deen et al., 2023; Gürsoy et al., 2022; Liu et al., 2018, 2019; W. Liu et al., 2018; Altunay and Elik, 2022; Shahvalinia et al., 2022; Barbayanov et al., 2022). Moreover, DESs have applications in many fields, such as synthesis of materials (Castro-Muñoz et al., 2022a,b) chemical tuning of biomaterials (Khajavian et al., 2022), food analysis (Haq et al., 2022), pharmaceuticals extraction (Faraz et al., 2021), molecular separations (Castro-Muñoz et al., 2022a,b), and bioactive extractions (Serna-Vázquez et al., 2021).

This research aims to develop an accessible and inexpensive method for selective and accurate microextraction of propineb from waters and foods. For this purpose, six DESs were prepared and added to real samples, and an ultrasound-assisted dispersive liquid-liquid microextraction based on solidification of floating organic drop (UA-DLLME-SFO) procedure was applied to extract propineb into a suitable DES solvent and remove sample interferences. Important variables were optimized by central composite design (CCD). The validation parameters of the method were investigated in detail. Obtained experimental results showed that 8-hydroxyquinoline and pivalic acid binary eutectic mixtures can be considered as an effective alternative to conventional organic volatile solvents in the development of the UA-DLLME-SFO method. Following validation studies, the developed method was successfully applied to the selected samples, and satisfactory recoveries and low relative standard deviations for the analysis of propineb. The novelty of the UA-DLLME-SFO-DES procedure are: 1) minimization of solvents and waste, and 2) the use of UV/VIS instead of expensive and energy-intensive analytical equipment such as GC/MS and LC/MS. Moreover, it has been shown for the first time that a deep eutectic solvent prepared from a mixture of 8-hydroxyquinoline and pivalic acid is applicable for the extraction of propineb.

2. Materials and methods

2.1. Instrumentation

In this research, the instruments used for the extraction and determination of propineb are given below. pH adjustment of the solutions was carried out using Metrohm 827 digital pH meter (Herisau, Switzerland). The sonication step was achieved using an ultrasonic bath (SK5210LHC model Kudos, Shanghai, China). The Design-Expert® software version 12.0.1 (Stat-Ease Inc., Minneapolis) was used for the optimization step and statistical analysis. Determination step were carried out by using an UV-1800 Shimadzu dual-beam spectrophotometer (Tokyo, Japan) coupled to 1.0-cm quartz cells (Fischer Scientific, USA). Ultra-pure water was obtained using Milli-Q water (Millipore, USA). A centrifuge (Hettich universal 320 model, Darmstadt, Germany) was used to ensure the separation of the phases.

2.2. Chemicals and reagents

All chemicals were of analytic grade. A stock solution of propineb (1000 mg L⁻¹) was prepared in DMSO using zinc propylenebis(dithiocarbamate) from Sigma (St. Louis, MO, USA). Working solutions were prepared by dilution of the stock solution. The acetate buffer solution (pH 4.6) was prepared by dissolving 5.4 g sodium acetate (Merck, Darmstadt, Germany) and 2.4 mL glacial acetic acid (Merck) in 100 mL water. In the preparation of DESs, methyltrioctylammoniumchloride (≥97.0%, MTOAC), hexafluoroisopropanol (≥99% HFIP), L-carnitine (≥98.0%), 1-octanol (≥99.0%), and salicylic acid (≥99.0%) was purchased from Sigma, while 8-

Hydroxyquinoline ($\geq 99\%$), menthol ($\geq 98.0\%$), pivalic acid ($\geq 99.0\%$), phenol ($\geq 99.0\%$) and levulinic acid ($\geq 98.0\%$) were purchased from Merk.

2.3. Sampling

The developed method was applied to two sample groups containing food and water samples. Tap water was as supplied from our lab. Well-water was collected from the agricultural area in Sivas/Türkiye. Waste water was collected from the industrial zone between September and November 2022 in Sivas/Türkiye. The spa water was collected from the hot spring region between October and December 2022 in Sivas/Türkiye. All water samples were filtrated through a $0.45 \mu\text{m}$ membrane filter and treated according to the UA-DLLME-SFO-DES procedure. Food samples including eggplant, cucumber, tomato, black tea, cereal-based baby food, fruit-based baby food, and infant formula powder were collected from local markets in Sivas. Food samples (50 g) were weighed using a digital balance and added to 250 mL beakers. Then, the water (200 mL) was added to the beakers. The mixture was vortexed for about 5 min. Then, the resulting mixture was filtered using a membrane filter and the UA-DLLME-SFO-DES procedure was applied to the obtained solutions.

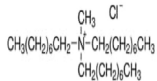
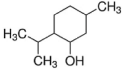
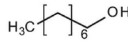
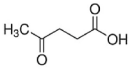
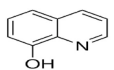
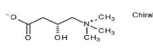
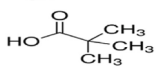
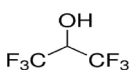
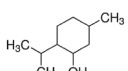
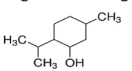
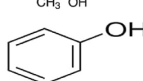
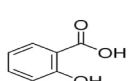
2.4. DES preparation

In this research, six DESs were prepared based on studies reported in the literature. The references, composition, molar ratio, and abbreviation of the prepared DESs are presented in Table 1. The following procedure was applied to the preparation of DESs. First, the HBA and the HBD components were added to the beaker in certain molar ratios. Afterward, the beakers were placed on the magnetic heating plate and heated at approximately $70\text{--}80 \text{ }^\circ\text{C}$ until a homogeneous liquid was obtained. The clear and homogeneous liquids obtained indicate that DESs have been prepared. The obtained liquids were used for experimental studies after cooling to room temperature. In this study, MTOAC, 8-Hydroxyquinoline, menthol and L-carnitine were used as HBA, while 1-octanol, pivalic acid, phenol, levulinic acid, HFIP and salicylic acid were used as HBD.

2.5. UA-DLLME-SFO-DES procedure

In this research, the UA-DLLME-SFO-DES procedure includes the following experimental steps. First, sample solution (5 mL) was added to the centrifuge tube including 100 ng mL^{-1} of propineb. The resulting solutions were then adjusted to pH 4.6 using acetate buffer solution. To achieve the extraction of propineb in the sample solution, $330 \mu\text{L}$ of DES-2 (prepared from the mixture of 8-Hydroxyquinoline and pivalic acid at molar ratio 1:2) was added to the resulting solution. To accelerate the mass transfer of propineb to the DES-2 phase, the centrifuge tube was then placed in an ultrasonic bath and sonicated for 1.5 min at $37.5 \text{ }^\circ\text{C}$. At this stage, the resulting solution became a turbid mixture. After centrifugation (4000 rpm 2 min), the DES-2 phase was separated and collected on the aqueous solution. Afterward, the centrifuge tube was left in an ice bath for 2 min to allow the DES-2 phase to solidify, the aqueous phase was evacuated. The final volume of the remaining phase was diluted to $500 \mu\text{L}$ using ethanol. For the determination step, the final solution was transferred into quartz cuvettes and placed in an UV-VIS spectrophotometer. Absorbance measurements were then carried out at 308 nm. All runs were performed in triplicate versus blank samples. The UA-DLLME-SFO-DES procedure is shown schematically in Fig. 1.

Table 1
The list of applications of DESs in extracting propineb.

Abbreviation	Component-1	Chemical structure-1	Component-2	Chemical structure-2	Molar ratio	References
DES-1	MTOAC		1-octanol		1:1	Tang et al. (2018)
DES-2	8-Hydroxyquinoline		pivalic acid		1:2	Mogaddam et al. (2020)
DES-3	Menthol		Phenol		1:1	Raj (2020)
DES-4	Menthol		Levulinic acid		1:1	Bezold and Minceva (2019)
DES-5	L-carnitine		HFIP		1:2	Deng et al. (2019)
DES-6	Menthol		Salicylic acid		4:1	Abri et al. (2019)

MTOAC: Methyltriocetyl ammonium chloride; HFIP: Hexafluoroisopropanol.

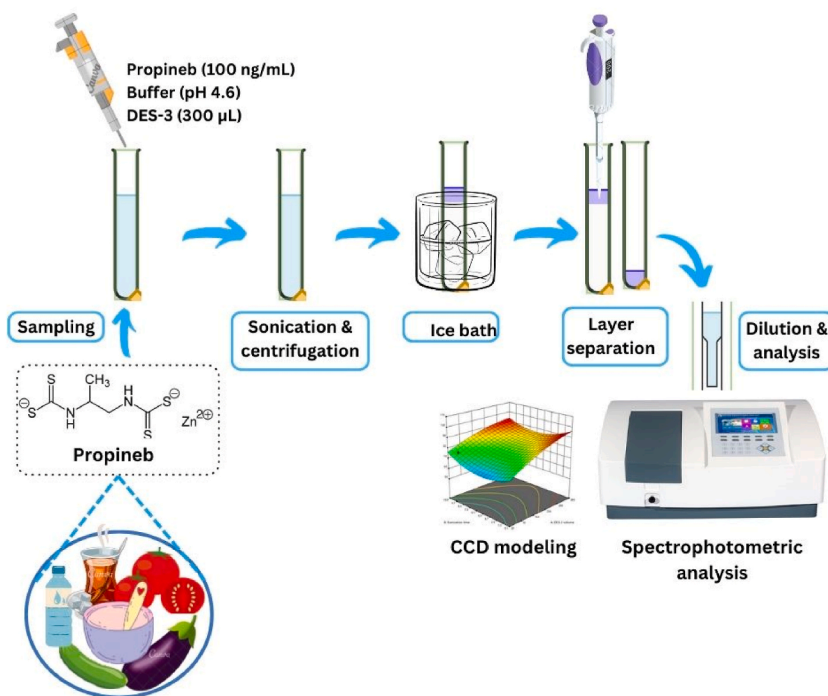


Fig. 1. The UA-DLLME-SFO-DES shown schematically.

2.6. Experimental modeling

Central composite design (CCD) is an impressive statistical method that is often applied to optimize important parameters in microextraction studies. In the study, four factors five-level CCD was applied for experiment design. Important parameters including DES-2 volume, sonication time, extraction temperature, and pH were coded with A (50–350 µL), B (1–10 min), C (25–60 °C), and D (3–8), respectively. Start points (\pm alpha) were applied as a control for all variables except the highest and lowest levels of the variables. A total of 30 experiments, including six central runs, were conducted. Information about experimental modeling is presented in Supplemental File Table S1.

2.7. Calculation of the average recovery

To optimize the variables, the average recovery was calculated as an analytical response according to the following equation-1.

$$\text{Average recovery (\%)} = \frac{n_{\text{final}}}{n_{\text{sample}}} \times 100 = \frac{C_{\text{final}} V_{\text{final}}}{C_{\text{sample}} V_{\text{sample}}} \times 100 \quad (1)$$

Where V_{final} and V_{sample} are the volumes of the final and sample solution, respectively. n_{sample} , n_{final} , C_{final} , and C_{sample} were total propineb, extracted propineb, the amounts of propineb in final phases, and the initial amount of propineb in the sample solution, respectively. C_{final} was calculated from a calibration curve, which was obtained using direct injection of model solutions.

3. Results and discussion

3.1. Effect of DES types

Extraction efficiency of the method to be developed depends on the nature of the prepared DES. Intermolecular interactions, physicochemical properties, and solubility of analytes can alter the method efficiency, which depends on the extraction solvent type. Therefore, six DESs were prepared and tested to ensure efficient and selective extraction of propineb. The effect of equal volumes of DESs prepared was examined at specific molar ratios on the recovery of propineb. According to the results in Fig. 2a, the recoveries obtained for DES-1, DES-2, DES-3, DES-4, DES-5 and DES-6 were 74.4%, 94.2%, 66.4%, 81.2%, 79.8% and 69.2%, respectively. According to these results, the best phase separation and good recoveries were obtained for DES-2, which consists of 8-hydroxyquinoline and pivalic acid. It is seen (Table 1) that there is the least steric barrier in DES-2. Accordingly, since it is easier to form H-bonds, eutectic mixture is obtained more easily than other DESs. Therefore, DES-2 was chosen as the suitable extraction solvent for the optimization step.

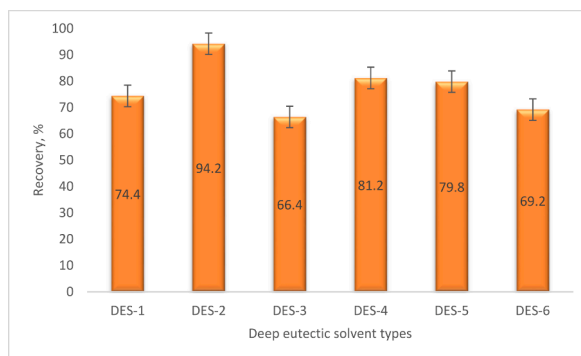


Fig. 2a. Effect of deep eutectic solvent types on recovery of propineb (N = 3).

3.2. Effect of molar ratio of DES-2

Once the appropriate extraction solvent has been selected, the molar ratio of its constituent components is an important factor affecting the effectiveness of the extraction solvent. Since DES is formed by hydrogen bonding between the components, the molar ratio of the components to the H-bond formation is affected. Therefore, DES-2-forming components 8-hydroxyquinoline and pivalic acid were prepared in different molar ratios and then their effect on the recovery of propineb was tested. According to the results in Fig. 2b, the recovery decreased as the molar ratio of 8-hydroxyquinoline in DES-2 increased. The highest recovery was obtained at 1:2 M ratio of 8-hydroxyquinoline and pivalic acid. In particular, as the molar ratio of pivalic acid in DES-2 decreases, the formation of eutectic mixture decreases. Therefore, the molar ratio of DES-2 was chosen as 1:2 for the optimization step.

3.3. Effect of NaCl amount

The addition of salt, which consists of small ions such as NaCl, causes the salting effect of the extraction solvents to shift the dispersion balance towards the anhydrous phases, thus maximizing the extraction efficiency. To evaluate the effect of this effect on the recovery of propineb, different concentrations (0.2, 0.4, 0.6, 0.8, 1.0, 1.25 and 1.5% (w/v)) of NaCl solution were added to the sample solution. From the results in Supplemental File Fig. S1, recovery of propineb was quantified in the absence of NaCl. Also, the added NaCl did not cause any significant changes in the recovery of propineb. Therefore, NaCl solution was not used in the optimization step.

3.4. Effect of mixing type

In order to provide effective and good phase separation, the extraction solvent must be completely dispersed in the sample solution. To achieve this, an appropriate mixing step is required after the extraction solvent is added to the sample solution. Based on these explanations, after adding the extraction solvent to the sample solution, different mixing types such as vortex, sonication, rotator, and hand shaking were applied to the tubes to ensure dispersion. According to the results in Fig. 2c, the recovery of propineb for vortex, sonication, rotator, and hand shaking mixing type was 78.9%, 94.2%, 70.3% and 61.2%, respectively. Obtaining the best phase separation in sonication can probably be attributed to the cavitation effect caused by sonication. Therefore, sonication was chosen as the appropriate mixing type in the optimization step.

3.5. Effect of sample volume

With an increase in sample volume, the analyte concentration will decrease and the efficiency of the method may change. For this reason, it is necessary to determine at which sample volumes the developed method provides maximum quantitative recovery. The ef-

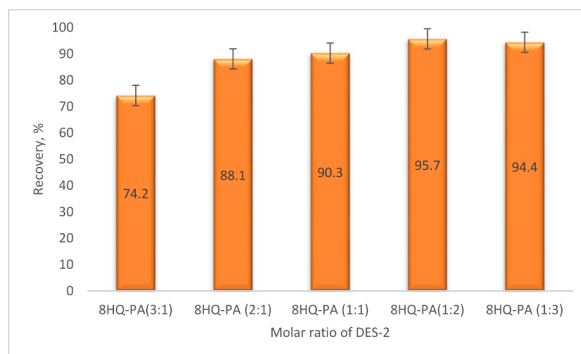


Fig. 2b. Effect of molar ratio of DES-2 on recovery of propineb (N = 3).

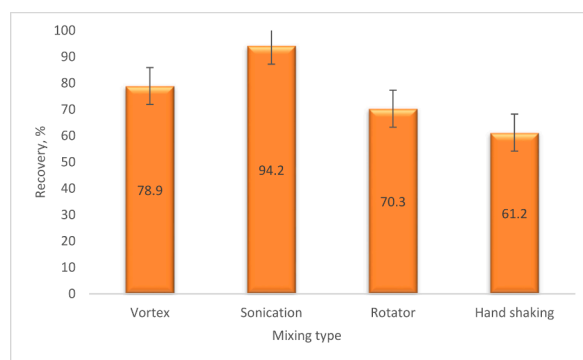


Fig. 2c. Effect of mixing type on recovery of propineb (N = 3).

fectiveness of the developed method was investigated in different sample volumes such as 15, 30, 45, 60, 75, 90, 100, 125, and 150 mL. Studies showed that there was no significant change in the recovery of propineb when the sample volume was increased from 15 mL to 60 mL. The recovery of propineb in this range of volumes was over 90%. However, recoveries of propineb were rapidly decreased after sample volumes beyond 60 mL. Since the concentration of propineb decreases depending on the increase in the volume of the sample solution, the extraction capacity of the developed method decreases at low concentrations. Accordingly, the recovery of propineb decreased as the sample volume increased. Therefore, the sample volume was chosen as 60 mL.

3.6. Optimization of UA-DLLME-SFO-DES procedure using CCD

The experimental design obtained from the CCD and the data obtained as a result of the application of this design were given in Table S2. The statistical evaluation obtained from the processing of the data in Table S2 was explained in detail below.

3.6.1. Statistical results

Statistical evaluations were made for the reliability of the results obtained from the optimization step. In this context, ANOVA results including statistical evaluations were presented in Table 2. First, the p-value should be less than 0.05 at the 95% confidence level for the CCD for the optimization step to be meaningful. The same definition also applies to variables and their interactions to be meaningful. According to Table 2 results, it is seen that the CCD and all interactions were significant for the recovery of propineb. Another explanation was to evaluate the contribution of the variables to the recovery of propineb. Accordingly, the larger the F-value for variables and interactions, the greater the contribution to the CCD. According to the data in Table 2c, the linear, binary, and quadratic interactions that contributed the most to the CCD were DES-2 volume (F-value: 3470.88), extraction temperature*DES-2 volume (F-value: 4900.74), and (sonication time)² (F-value: 2332.29), respectively. A “Lack of Fit p-value” of 0.8884 means that it is not significant relative to the pure error. Furthermore, the effect of the optimized variables on the recovery of propineb was explained with the following quadratic equation-2.

$$\text{Recovery (\%)} = +79.53 + 3.79A - 1.59B - 0.2362C - 2.26D - 1.31AB + 4.89AC - 0.1687AD - 1.79 BC - 3.81BD - 2.23CD - 2.30A^2 + 5.93 B^2 - 1.05C^2 - 3.48D^2 \quad (2a)$$

Table 2
Statistical analysis results of CCD.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1416.47	14	101.18	1294.01	<0.0001	significant
A-DES-2 volume	271.38	1	271.38	3470.88	<0.0001	
B-Sonication time	47.99	1	47.99	613.75	<0.0001	
C-Extraction temperature	1.05	1	1.05	13.47	0.0023	
D-pH	96.39	1	96.39	1232.81	<0.0001	
AB	27.30	1	27.30	349.16	<0.0001	
AC	383.18	1	383.18	4900.74	<0.0001	
AD	0.4556	1	0.4556	5.83	0.0290	
BC	51.48	1	51.48	658.42	<0.0001	
BD	231.80	1	231.80	2964.64	<0.0001	
CD	79.66	1	79.66	1018.77	<0.0001	
A ²	27.34	1	27.34	349.72	<0.0001	
B ²	182.36	1	182.36	2332.29	<0.0001	
C ²	5.68	1	5.68	72.67	<0.0001	
D ²	62.67	1	62.67	801.57	<0.0001	
Lack of Fit	0.5328	10	0.0533	0.4163	0.8884	not significant
R ²		0.9992	Predicted R ²		0.9967	
Adjusted R ²		0.9984	Adeq Precision		167.5467	

Quality factors including R^2 , adjusted- R^2 , predicted- R^2 , and adeq-precision should be investigated for the reliability of the obtained analytical results using the CCD. R^2 value close to 1.0 was desirable for reliable results. R^2 represents the variation of the obtained analytical data around the mean and was equal to 0.9992. Adjusted- R^2 (0.9984) adjusts the number of variables contributing to the CCD and decreases as the number of variables in the CCD increases. This value was statistically acceptable at $p < 0.05$, indicating a good correlation between the experimental results and the CCD. Sufficient sensitivity was a signal-to-noise ratio. Compares the experimental results with the estimated range of values with the mean prediction error. If the Adeq-precision (167.5467) was greater than 4, it indicates sufficient discrimination of the CCD. It was seen in Supplemental File Fig. S2, that the results obtained from the experimental studies have a high agreement with the predicted values of the CCD model.

3.6.2. Response surface plots

Response surface plots were drawn to explain the effect of binary interactions of optimized variables on the recovery of propineb. First, the effect of DES-2 volume and sonication time on the recovery of propineb was given in Fig. 3a. Acceptable recoveries were achieved at low and high sonication times, especially when the DES-2 volume was above 275 μL . The low recovery of propineb at low DES-2 volumes was due to the insufficient amount of extraction solvent required for phase separation. The sonication application helped to ensure rapid mass transfer of DES-2 molecules to the sample solution. The effect of extraction temperature and DES-2 volume on the recovery of propineb was given in Fig. 3b. Since temperature increases the kinetic energy of DES-2 molecules, it accelerates its dispersion in the sample solution. Quantitative recovery above 55 $^\circ\text{C}$ could not be achieved. The main reason for this may be the degradation of DES-2 molecules with the increase in temperature. In addition, phase separation could not be achieved at temperatures below 30 $^\circ\text{C}$, due to the decrease in mass transfer rate of DES-2 molecules. The effect of pH and DES-2 volume on the recovery of

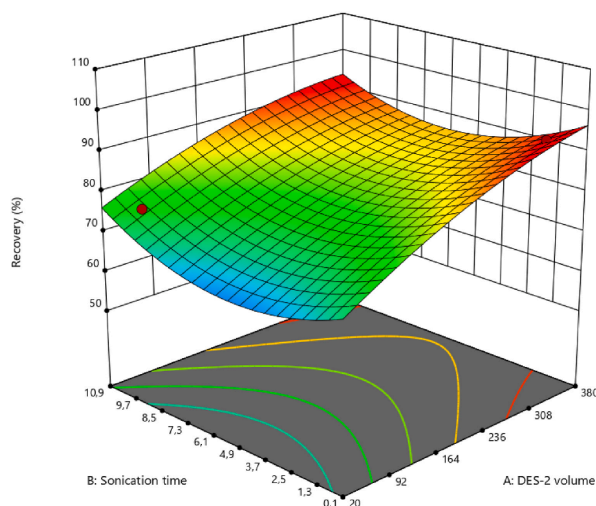


Fig. 3a. The effect of sonication time and DES-2 volume on the recovery of propineb (N = 3).

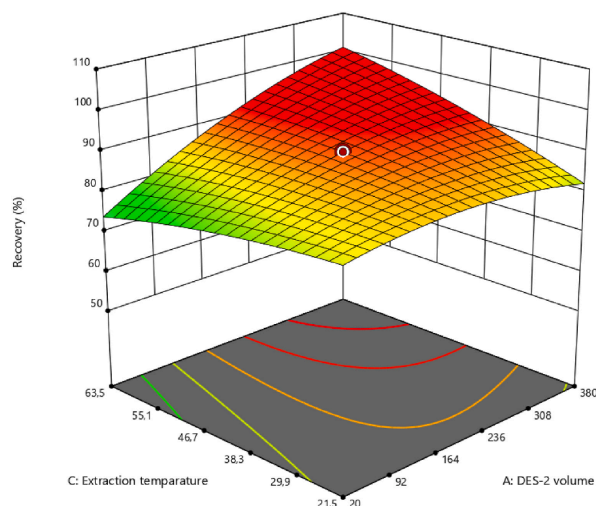


Fig. 3b. The effect of extraction temperature and DES-2 volume on the recovery of propineb (N = 3).

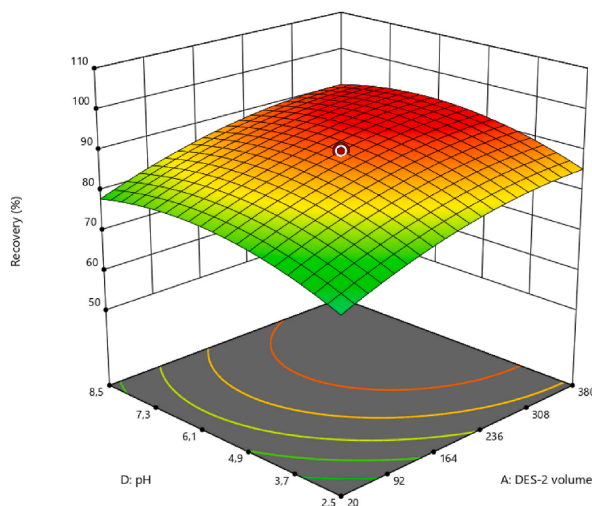


Fig. 3c. The effect of pH and DES-2 volume on the recovery of propineb (N = 3).

propine was given in Fig. 3c. Recovery of propineb was quantitative when pH was in the range of 3.8–7.3 and DES-2 volume was in the range 270–350 μL , respectively. Phase separation could not be achieved at low pH, which may be due to excessive protonation of DES-2 in the acidic medium.

3.6.3. Optimum conditions

Based on the CCD results, the best recovery of propineb was calculated as 93.1% with DES-2 (330 μL), sonication time (1.5 min), extraction temperature (37.5 $^{\circ}\text{C}$) and pH (4.6). For the reliability of the optimization step of the CCD, the optimum values of the studied parameters were chosen when the desirability was 1. Five repetitive runs were conducted using these conditions predicted by the CCD model for the selected variables. The recovery of propineb from the studies was calculated as 92.6%. The result obtained was statistically acceptable and had a high agreement with the predicted value. Therefore, these conditions for the variables were chosen as optimum for validation studies and analysis.

3.7. Method performance

After the CCD steps, the UA-DLLME-SFO-DES procedure was observed a linear range for 20–450 ng mL^{-1} of propineb, determined by the calibration curve $A = 0.0074-0.015$ [propineb, ng mL^{-1}] ($R^2 = 0.995$), which A was the absorbance. Limit of detection (LOD) and limit of quantification (LOQ) were considered as S_{blank} to slope (m) ratios of 3 and 10, respectively. Where m was the slope of the resulting calibration plot, while S_{blank} was the standard deviation of twelve replicate measurements of the sample blank. The LOD and LOQ of the UA-DLLME-SFO-DES procedure were 6.1 ng mL^{-1} and 20 ng mL^{-1} , respectively. The preconcentration factor (PF) (120) was calculated from the ratio of the sample volume (60 mL) to the measurement volume (0.5 mL). The enrichment factor (EF) (93) was calculated from the ratio of the slopes of the calibration graphs obtained before and after the UA-DLLME-SFO-DES procedure. Moreover, the recovery and relative standard deviation (RSD%) calculated from eleven replicate measurements of 75 ng mL^{-1} of propineb were 97.4% and 1.9%, respectively. The described results were presented in detail in Table 3.

Table 3

Some analytical figures of the presented method.

Analytical figures	Values
Calibration curve	$A = 0.0074$ [propineb, ng mL^{-1}] - 0.015
Correlation coefficient (R^2)	0.995
Linear range (ng mL^{-1})	20–450
Limit of detection ($3S_{\text{blank}}/m$, ng mL^{-1})	6.1
Limit of quantification ($10S_{\text{blank}}/m$, ng mL^{-1})	20
^a Preconcentration factor (PF)	120
^b Enrichment factor (EF)	93
^a RSD (%)	1.9
^a Recovery (%)	97.4

^a $\text{PF} = V_{\text{final volume}}/V_{\text{sample volume}}$ (Where $V_{\text{final volume}}$ is the final volume obtained after the UA-DLLME-SFO-DES procedure, while $V_{\text{sample volume}}$ is the volume of the sample solution used).

^b $\text{EF} = m_1/m_2$ (where m_1 and m_2 are the slopes of the calibration graphs obtained before and after the UA-DLLME-SFO-DES procedure, respectively).

^c for eleven replicate measurements of 75 ng mL^{-1} of propineb.

3.8. Selectivity

Since the optimization step was performed using model solutions, the selectivity of the UA-DLLME-SFO-DES procedure should be investigated before the analysis of real samples. Matrix species in real samples can affect the extraction of propineb, causing variations in the analytical signals. Therefore, the selectivity of the UA-DLLME-SFO-DES procedure was investigated by adding matrix species shown in Table 4 to the model solutions at different rates. The tolerance limit was calculated from the ratio of the concentration of the matrix species, which causes a $\pm 5\%$ change in the analytical signal, to the concentration of propineb. The tolerable limits of the method were 7500 for Na^+ and Mg^{2+} ions, 500 for Ca^{2+} , K^+ , Cl^- , SO_4^{2-} and NH_4^+ ions, 2500 for Mn^{2+} and CO_3^{2-} ions, 1000 for Ni^{2+} and Cr^{3+} ions, 500 for NO_3^- and Hg^{2+} ions, 250 for Co^{2+} and Pb^{2+} ions, 100 for Cd^{2+} , ferbam and zineb and 50 for maneb and mancozeb. In addition, the RSD% and recovery in the presence of the matrix species were in the range of 1.1–2.4% and 91 ± 6 – $99 \pm 2\%$, respectively. All these results showed that the UA-DLLME-SFO-DES procedure exhibits high selectivity even in the presence of matrix species.

3.9. Accuracy and precision

Intra-day and inter-day precision and accuracy of the UA-DLLME-SFO-DES procedure were evaluated by analyzing six replicates at three different amounts of quality control samples under the optimum extraction conditions. Quality control samples at low (30 ng mL^{-1}), medium (250 ng mL^{-1}), and high (400 ng mL^{-1}) concentrations of propineb were analyzed on the same day (intra-day studies) and six different days (inter-day studies). The obtained data in terms of recovery and RSD% were given in Table 5. The RSD% for intra- and inter-day studies were in the range of 1.4–1.9% and 1.7–2.8%, respectively. Moreover, recoveries for intra- and inter-day studies were in the range of 93.3–98.1% and 90.3–95.5%, respectively. The data obtained from these studies showed that the UA-DLLME-SFO-DES procedure was accurate and precise.

3.10. Robustness

Robustness was expressed as the capacity to produce unbiased results in the presence of small changes in optimized microextraction conditions. In this step, the optimized variables were changed by $\pm 15\%$. When changing a variable, the optimized values of the other variables were used. As a result of the experiments, the recovery and RSD% of propineb were obtained in a range of 92.9–97.5% and 1.9–2.8%. Obtained analytical results confirmed the robustness of the UA-DLLME-SFO-DES procedure.

Table 4
Selectivity of the presented method in the presence of matrix species.

Matrix species	RSD (%)	Recovery (%)	Tolerable limit ^a
Na^+	1.4	99 ± 2	7500
Mg^{2+}	1.7	99 ± 1	7500
Ca^{2+}	1.6	98 ± 3	5000
K^+	1.3	98 ± 2	5000
Cl^-	1.8	97 ± 4	5000
SO_4^{2-}	1.6	98 ± 1	5000
NH_4^+	1.4	98 ± 2	5000
Mn^{2+}	1.9	97 ± 3	2500
CO_3^{2-}	1.6	97 ± 4	2500
Ni^{2+}	1.3	97 ± 2	1000
Cr^{3+}	1.2	96 ± 3	1000
NO_3^-	1.1	96 ± 4	500
Hg^{2+}	1.8	96 ± 4	500
Co^{2+}	1.2	96 ± 3	250
Pb^{2+}	1.9	95 ± 3	250
Cd^{2+}	2.0	93 ± 4	100
Ferbam	1.7	94 ± 6	100
Zineb	1.6	92 ± 4	100
Maneb	2.4	92 ± 7	50
Mancozeb	2.1	91 ± 6	50

^a [Amount of matrix species, ng mL^{-1}]/[Amount of propineb, ng mL^{-1}].

Table 5
Assay precision and accuracy of quality control samples.

Studies	Spiked concentration (ng mL^{-1})	Calculated concentration (ng mL^{-1})	Recovery (%)	Average of recovery %	RSD (%)	Average of RSD %
Intra-day assay (N = 6)	30	27.9	93.0	95.8	1.4	1.7
	250	241.0	96.4		1.8	
	400	392.4	98.1		1.9	
Inter-day assay (N = 6 × 3)	30	27.1	90.3	93.4	1.7	2.2
	250	235.8	94.3		2.1	
	400	382.0	95.5		2.8	

3.11. Application of the UA-DLLME-SFO-DES procedure for analysis of propineb in water and food samples

Following validation studies, the UA-DLLME-SFO-DES procedure was applied to two sample groups containing water and food. Propineb could not be detected in the analyzed water samples including tap water, well water, wastewater, and spa water. To check the accuracy of the method in the analysis step, two concentrations of propineb (30 and 120 ng mL⁻¹) were added to the water samples and extracted by the UA-DLLME-SFO-DES procedure. Results were reported as recovery in Table 6a. The recovery was calculated according to the following equation (Gao et al., 2012);

$$\text{Recovery (\%)} = \frac{\text{Change in the amount of analyte measured}}{\text{Amount of analyte added to the sample solution}} \times 100 \quad (2b)$$

The recoveries from the analysis of water samples ranged from 93.7% to 98.6%. The data shows that the UA-DLLME-SFO-DES procedure can be considered an efficient and reliable method for the extraction of propineb in different water and food samples, where the matrix of the samples does not have a significant effect on the UA-DLLME-SFO-DES procedure efficiency.

To evaluate the accuracy of the UA-DLLME-SFO-DES procedure, 8 mg kg⁻¹ of propineb was added to the food samples while the developed method was applied to these samples. According to the results in Table 6b, the highest and lowest amounts of propineb in the analyzed food samples were found in cereal-based baby food (8.35 ± 0.38 mg kg⁻¹) and tomato (1.14 ± 0.09 mg kg⁻¹), respectively. The results obtained were below the acceptable limits of the WHO. Moreover, the quantitative recoveries showed that the UA-DLLME-SFO-DES procedure exhibits high accuracy in complex matrices.

3.12. Comparison of the UA-DLLME-SFO-DES and other methods

Some analytical figures of the UA-DLLME-SFO-DES procedure were compared with other reported methods (Song et al., 2018; Bodur et al., 2020; Soylak et al., 2022; Vaclavik et al., 2018; Öter and Zorer, 2022; Jouyban et al., 2020). In addition, a detailed com-

Table 6a

Application results of the presented method to water samples (N = 5).

Water samples	Spiked, ng mL ⁻¹	Found, ng mL ⁻¹	Recovery (%)	*Matrix effect (%)
Tap water	–	ND ^a	–	3.9
	30	29.2 ± 0.9 ^b	97.3	
	120	118.3 ± 3.7	98.6	
Well water	–	ND	–	4.5
	30	28.1 ± 1.1	93.7	
	120	114.7 ± 2.6	95.6	
Waste water	–	ND	–	4.2
	30	28.4 ± 0.7	94.7	
	120	115.7 ± 2.4	96.4	
Spa water	–	ND	–	7.1
	30	28.7 ± 1.0	95.7	
	120	116.8 ± 2.8	97.3	

^a Not detected.

^b Mean ± standard deviation.

^c It is described as % Matrix effect = (m' - m₀)/m₀ × 100 with acceptable signal enhancement, where m' and m₀ are slopes of two calibration curves (model solutions and the matrix-matched solutions), respectively.

Table 6b

Application results of the presented method to food samples (N = 5).

Food samples	Spiked, mg kg ⁻¹	Found, mg kg ⁻¹	Recovery (%)	*Matrix effect (%)
Eggplant	–	1.7 ± 0.1**	–	8.2
	8	9.1 ± 0.7	92.5	
Cucumber	–	3.6 ± 0.1	–	6.9
	8	11.2 ± 0.8	95.0	
Tomato	–	1.1 ± 0.1	–	10.3
	8	8.4 ± 0.7	91.3	
Black Tea	–	5.8 ± 0.1	–	7.6
	8	13.6 ± 0.9	97.5	
Cereal-based baby food	–	8.4 ± 0.4	–	11.5
	8	16.1 ± 0.9	96.3	
Fruit-based baby food	–	4.3 ± 0.3	–	9.4
	8	11.7 ± 0.8	92.5	
Infant formula powder	–	2.0 ± 0.2	–	8.8
	8	9.6 ± 0.6	95.0	

* It is described as % Matrix effect = (m' - m₀)/m₀ × 100 with acceptable signal enhancement, where m' and m₀ are slopes of two calibration curves (model solutions and the matrix-matched solutions), respectively.

** Mean ± standard deviation.

Table 7
Comparative study table for propineb analysis methods.

Extraction method	Analytical method	LOD	Linearity range	RSD%	Matrix	References
¹ DES-SA-LPME	Spectrophotometry	6.1 ng mL ⁻¹	20–450 ng mL ⁻¹	2.8	Water and food	<i>Present method</i>
Co-precipitation	FAAS	15.2 ng mL ⁻¹	5000–70000 ng mL ⁻¹	3.1	Vegetables	Soylak et al. (2022)
QuEChERS	GC-MS	10–50 ng mL ⁻¹	–	0.47–6.47	Tomato	Tripathy et al. (2021)
DLLME	GC-MS	150 mg kg ⁻¹	0.50 and 20 mg kg ⁻¹	9.4	Black tea, infant formula	Bodur et al. (2020)
QuEChERS	Luminescence	30 ng mL ⁻¹	100–2000 ng mL ⁻¹	5	Capers	Ruiz-Medina et al. (2022)
² DES-ATE	Absorbance microplate reader	0.6 µg kg ⁻¹	0.6–6000 µg kg ⁻¹	4.2	Foods	Guo et al. (2023)
Modified QuEChERS	LC-MS	3 µg kg ⁻¹	0.075–1.5 ng mL ⁻¹	13	Baby food	Vaclavik et al. (2018)

¹DES-SA-LPME: Deep eutectic solvent-based sonication-assisted liquid phase microextraction.

²DES-ATE: Deep eutectic solvent-based adhesive tape extraction.

parison of the method with different techniques was presented in Table 7. The UA-DLLME-SFO-DES procedure has low LOD (6.1 ng mL⁻¹), wide linearity range (20–450 ng mL⁻¹), and comparable RSD (1.9%) as compared to other analytical procedures. In addition, the extraction time (4 min) of the method was shorter than the other methods and also the preconcentration factor (120) was higher. Obtained results were acceptable for an analytical approach to be recognized as an efficient, sensitive, and robust technique for the analysis of propineb in water and food samples.

3.13. Greenness assessment

The main purpose of the concept of green chemistry, which emerged in the early 1990s, is to reduce or eliminate the use/production of toxic chemicals. The eco-scale evaluation procedure is based on penalty scores subtracted from a base of 100 (Zhang et al., 2022). The penalty points are awarded for each type and amount of reagent that may cause environmental problems, the analyst's possible occupational exposure, the amount of energy consumed by electrical equipment, and the analytical method. Excellent green analysis should have an eco-scale score of >75, an acceptable green analysis score of >50, if the method scores <50, it will be considered an unsatisfactory green analysis. The penalty score for different aspects of the developed method was calculated as 72. Based on the explanations, the proposed method is considered the acceptable green method.

4. Conclusion

In this study, an analytical methodology based on the UA-DLLME-SFO-DES procedure followed by UV-VIS spectrophotometer was optimized for the determination and extraction of propineb in water and food samples. The CCD was used to optimize the main parameters affecting the recovery of the propineb. The optimized conditions were sufficient for the selective quantification of propineb, minimizing waste generation as well as reagents and sample consumption. The main advantage of the UA-DLLME-SFO-DES procedure was the use of DES as the extraction solvent in the extraction step which led to the elimination of toxic organic solvents. The UA-DLLME-SFO-DES method has a low LOD (6.1 ng mL⁻¹), wide linear range (20–450 ng mL⁻¹), high precision (RSD ≤1.9%), PF (120) and good matrix effect (3.9–11.5%). Combined with other analytical methods, this method shows satisfactory added recovery (91.3–198.6%) for the detection of propineb in water and food samples. The strengths of the UA-DLLME-SFO-DES procedure are: 1) minimization of solvents and waste, 2) the use of UV/VIS instead of expensive and energy-intensive analytical equipment such as GC/MS and LC/MS, and 3) the use for routine monitoring of propineb in complex matrices. Finally, these prepared DESs have the potential to be applied to the separation and enrichment of organic and inorganic species in real samples.

Author contributions section

Adil Elik: Supervision, Sampling, Writing - review & editing., Nail Altunay: Investigation, Validation, Writing -original draft.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scp.2023.101215>.

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