

ULTRASOUND-ASSISTED DIGESTION USING CHOLINE CHLORIDE-OXALIC ACID DEEP EUTECTIC SOLVENT FOR MACRO AND MICROELEMENTS DETERMINATION IN RICE BY ICP-OES**

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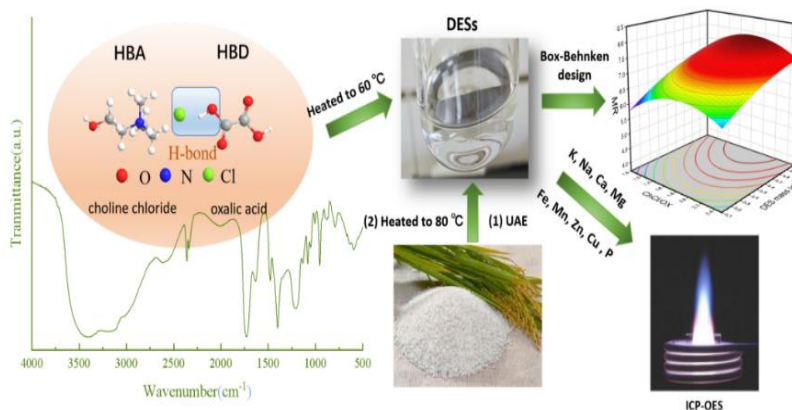
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The incessant generation of toxic waste and growing environmental concerns have prompted the scientific community to conduct comprehensive research in order to discover more sustainable analytical techniques. In this context, the application of deep eutectic solvents (DESs) has become one of the main strategies in green chemistry. In this work, a rapid, simple, and environmentally friendly method was developed for the extraction of K, Na, Ca, Mg, Fe, Mn, Cu, Zn and P from rice samples using ultrasound-assisted deep eutectic solvents. The determination of target analytes in the extracts was performed using inductively coupled plasma-optical emission spectrometry (ICP-OES). The response



surface methodology (RSM), based on the Box-Behnken design, was employed to determine the optimal conditions of the significant parameters. Under optimized conditions, the limits of detection (LOD) and limits of quantification (LOQ) ranged from 0.037 to 1.322 $\mu\text{g g}^{-1}$ and from 0.122 to 4.406 $\mu\text{g g}^{-1}$, respectively. The analysis results of the reference samples revealed a relative error (RE) ranging from -6.6% to -3.8%, while the relative standard deviation (RSD) remained below 5.5%. These findings demonstrate excellent accuracy and precision. F-test and t-test results indicated that, at a 95% confidence level, there was no statistically significant difference between the accuracy and precision of the method proposed in this study and the microwave digestion method for determining actual rice samples. The proposed method exhibits advantages over classical microwave-assisted digestion procedures based on concentrated acids, considering critical parameters such as cost, green chemistry, and analyst safety.

INTRODUCTION

The consumption of rice, which is a significant source of starch, protein, and various essential

nutrients, contributes to the nutritional needs of over 50% of the global population and plays a pivotal role in promoting human health. Mg, Na, and K are essential for maintaining pH, osmotic pressure, and

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nerve conductivity. Ca and P contribute to bone formation. Cu, Zn, Fe, and Mn play important roles in respiratory processes and the immune system.¹

The determination of elements in plant samples typically entails intricate sample preparation procedures, followed by quantitative analysis employing analytical techniques.²⁻⁴ The majority of pre-treatment procedures involve the utilization of hazardous chemicals, including concentrated sulfuric acid, hydrochloric acid, nitric acid, and hydrogen peroxide.^{5,6} The emission of vapors into the atmosphere resulting from the utilization of hazardous chemicals poses a significant health risk to analysts and causes environmental harm. Therefore, the development of more cost-effective and environmentally friendly sample preparation methods is an imperative task in analytical chemistry.

Recently, a novel category of environmentally sustainable solvents known as deep eutectic solvents (DESs) has been introduced in the field of analytical chemistry for sample pretreatment.^{7,8} DESs exhibit non-flammability, low volatility, excellent biocompatibility, and low toxicity, making them an ideal choice for environmentally friendly solvents. Additionally, the vast array of potential components and combinations make DESs remarkably versatile and easily synthesized.⁹⁻¹² DESs are characterized as mixtures of at least two substances, namely a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), which interact through hydrogen bonds resulting in a significantly lower melting point compared to that of either individual component.¹³ Choline chloride is the most commonly utilized HBA, while monohydric and polyhydric alcohols, carboxylic acids, and urea can serve as suitable HBDs.^{10,14} DESs can serve as analogues of potent oxidizing mixtures containing concentrated nitric acid and hydrogen peroxide for the purpose of sample decomposition. The aforementioned statement will facilitate the future development of rapid and environmentally friendly methodologies for decomposing samples containing diverse components, thereby eliminating the necessity for corrosive solvents. DESs have demonstrated utility in the separation of organic analytes and metals from various matrices, including food, plants, water samples, and edible oils.¹⁵⁻²⁰

Extraction is a fundamental step in sample preparation, and optimal extraction parameters can be employed in conjunction with ultrasound-

assisted extraction (UAE)^{21,22} or microwave-assisted extraction (MAE)^{23,24} to achieve satisfactory outcomes. The UAE technique is regarded as one of the most promising extraction technologies due to its ability to utilize smaller volumes of solvents and achieve shorter extraction times. Moreover, it aligns perfectly with the principles of green chemistry, enabling faster and simpler sample preparation.^{25,26} The extraction process in UAE technology involves the utilization of ultrasonic energy, thereby facilitating enhanced contact between the sample and the extraction solvent. Moreover, UAE can effectively facilitate deeper penetration of the extracting solvent into solid sample matrices.²⁷ Due to the efficacy of UAE technology in analyzing diverse samples, there is a growing interest in its application for rapid and efficient extraction of analytes.²⁸ Currently, DES-based UAE is predominantly employed for the isolation of organic compounds, with limited application in extracting plant samples or inorganic analytes.²⁹⁻³¹

At present, the most effective methods for the target analytes of plant samples are flame atomic absorption spectrophotometry (FAAS),^{18,21,32} graphite furnace atomic absorption spectrometry (GFAAS),^{19,32} inductively coupled plasma emission spectroscopy (ICP-OES),^{33,34} inductively coupled plasma mass spectrometry (ICP-MS)^{10,35} and X-ray fluorescence spectroscopy (XRF).^{36,37} FAAS and GFAAS are highly sensitive single element analysis methods. XRF is a rapid and non-destructive method for multi-elemental analysis, however it is unsuitable for determining trace elements. Additionally, it is susceptible to matrix effects and necessitates the use of numerous reference materials with similar matrices for correction purposes. ICP-OES and ICP-MS are widely employed multi-elemental analysis techniques, characterized by high sensitivity, broad linear dynamic range, and rapid analytical speed. However, ICP-MS is not a suitable analytical technique for the determination of high concentration elements such as K, Ca, Mg and P in plant samples.

In light of the aforementioned, this study aims to develop an ultrasound-assisted deep eutectic solvent (DES) extraction method for quantifying K, Na, Ca, Mg, Fe, Mn, Cu, Zn and P in rice samples. The DESs based on choline chloride and oxalic acid were synthesized as an appropriate solvent system for the extraction of target analytes from rice samples, followed by their determination using ICP-OES.

RESULTS AND DISCUSSION

Synthesis and characterization of the DESs

The formation of DESs can be confirmed by means of FT-IR spectroscopy (Fig. S1). A noticeable shift in the vibrational band was observed within the 3000–3500 cm^{-1} spectral region of the synthesized DESs, providing evidence for the establishment of hydrogen bonding interactions between choline chloride and oxalic acid. The band observed at 1632 cm^{-1} can be attributed to the angular deformation of -OH groups in water molecules present within the DESs. The absorption band corresponding to the stretching of C=O of oxalic acid was observed at 1728 cm^{-1} , which exhibited a redshift from its initial position at 1684 cm^{-1} . This spectral shift signifies the occurrence of

intermolecular hydrogen bonding between these reactants. The elongation in wavelength associated with carbonyl stretching implies an augmentation in electron density on the carbonyl oxygen, indicative of hydrogen bond formation.

Model equation and significance test

The efficiency of ultrasonic extraction was assessed based on the ratio of ChCl/OX, mass of DES, and duration of ultrasonication. A Box–Behnken design was employed to optimize the digestion procedure, utilizing a quadratic model for identifying the optimal conditions. The multiple responses (MR) was utilized to execute the Box–Behnken design. The obtained results from this experimental design are presented in Table 1, along with the corresponding response surface depicted in Fig. 1.

Table 1

Box–Behnken design for multivariate optimization of rice sample digestion

Experiment	ChCl/OX	DES mass (g)	UAE time (min)	Extraction recovery (%)									MR
				K	Na	Ca	Mg	Fe	M _n	Cu	Zn	P	
1	1(-1)	0.1(-1)	25(0)	63	61	55	71	61	75	66	75	63	5.897
2	2.5(1)	0.1(-1)	25(0)	62	65	75	69	72	74	66	73	79	6.349
3	1(-1)	1(1)	25(0)	80	79	80	72	74	76	81	84	78	7.041
4	2.5(1)	1(1)	25(0)	78	86	71	75	83	81	79	89	80	7.230
5	1(-1)	0.55(0)	10(-1)	60	57	57	58	71	54	54	58	62	5.325
6	2.5(1)	0.55(0)	10(-1)	62	59	54	55	69	57	58	62	60	5.374
7	1(-1)	0.55(0)	40(1)	86	77	83	82	77	86	83	88	75	7.371
8	2.5(1)	0.55(0)	40(1)	90	85	75	89	92	91	96	93	79	7.908
9	1.75(0)	0.1(-1)	10(-1)	63	63	61	67	70	71	74	75	69	6.129
10	1.75(0)	1(1)	10(-1)	66	65	67	68	75	74	77	76	72	6.401
11	1.75(0)	0.1(-1)	40(1)	65	64	57	71	71	77	69	74	66	6.145
12	1.75(0)	1(1)	40(1)	95	97	103	104	93	98	105	104	102	9.000
13	1.75(0)	0.55(0)	25(0)	75	86	81	79	83	88	79	89	80	7.405
14	1.75(0)	0.55(0)	25(0)	77	85	79	82	82	85	78	88	81	7.374
15	1.75(0)	0.55(0)	25(0)	77	84	80	80	83	89	81	87	81	7.425
16	1.75(0)	0.55(0)	25(0)	78	85	81	82	82	86	78	91	79	7.424
17	1.75(0)	0.55(0)	25(0)	78	86	82	81	80	90	82	88	81	7.482

The test results presented in Table 1 were subjected to multiple linear regression analysis, yielding regression

equations for the following variables: MR, ChCl/OX ratio (A), DES mass (B), and ultrasonic time (C).

$$\text{MR} = 1.9061 + 3.8268 \cdot A + 0.3812 \cdot B + 0.05925 \cdot C - 0.1948 \cdot A \cdot B + 0.01084 \cdot A \cdot C + 0.09567 \cdot B \cdot C - 1.0817 \cdot A^2 - 0.9099 \cdot B^2 - 0.001418 \cdot C^2 \quad (1)$$

The results of the regression and variance analysis demonstrated that the regression model ($P=0.0006$) has achieved a highly significant level (Table S1). Moreover, the coefficient of

determination ($R^2=0.9563$) indicates an excellent fit of the equation, enabling its application for analytical element extraction analysis and prediction in rice.

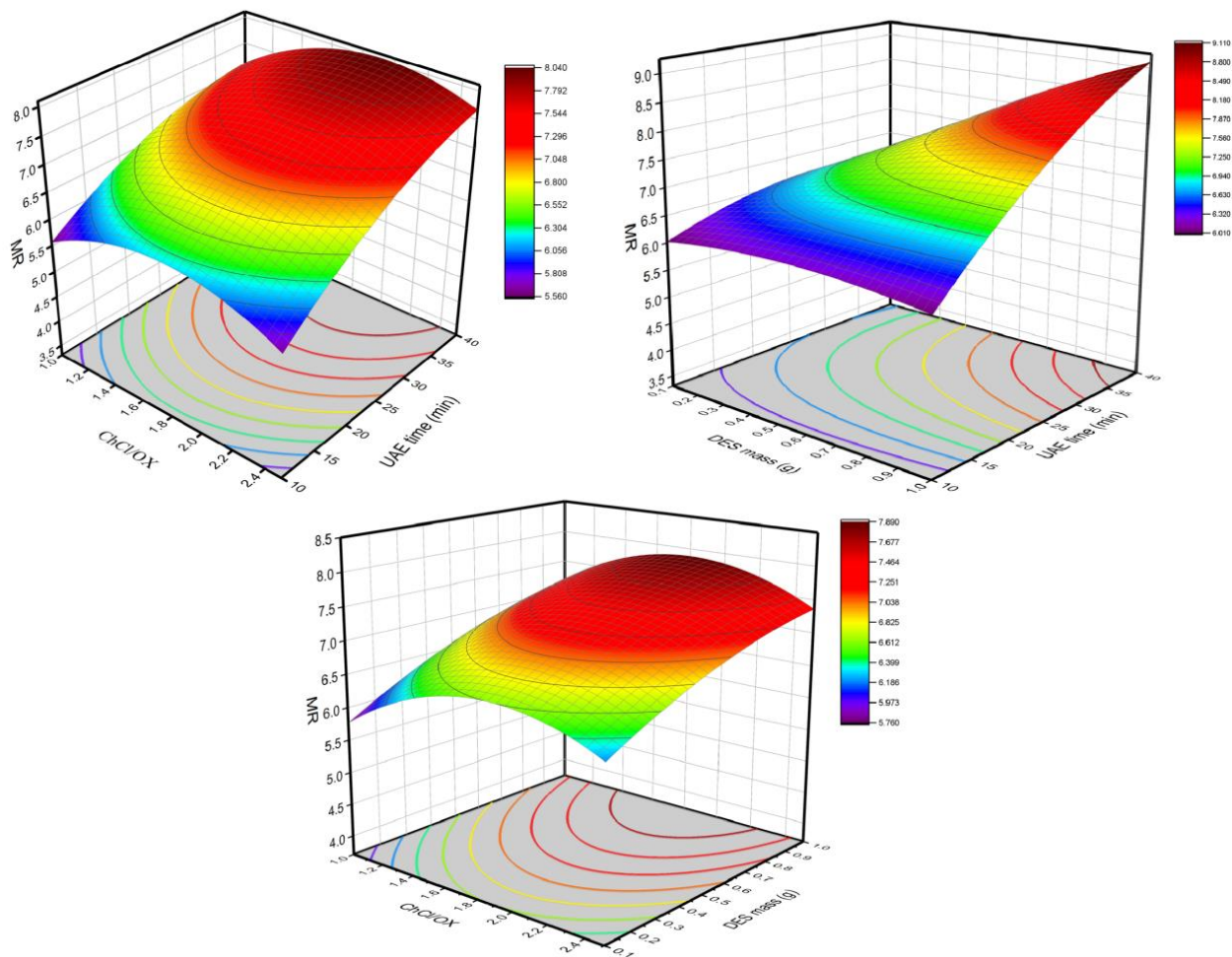


Fig. 1 – Response surface curves for the effects of ChCl/OX ratio, DES mass, and ultrasonic time in multiple responses obtained from the Box–Behnken design.

The interaction of various factors

The interaction between the mass of DES and the ChCl/OX ratio was not found to be statistically significant ($p=0.677$). When maintaining a constant ChCl/OX ratio, an increase in the mass of DES results in a corresponding elevation of the MR Value. However, when keeping the DES mass constant, MR Values initially rise and subsequently decline with increasing ChCl/OX ratios. With an increased concentration of oxalic acid, a higher number of protons within carboxylic acids function as oxygen acceptors, leading to the formation of chelating complexes between cations and carboxylic acids. However, an excessive quantity of

oxalic acid may adversely impact the stability of DESs, resulting in elevated melting point and viscosity values for the solution. Consequently, this can hinder both mass and solvent transfer rates during the extraction process.

The interaction between ultrasound exposure time and ChCl/OX ratio did not yield statistically significant results ($p=0.447$). Holding the ChCl/OX ratio constant, longer ultrasound exposure resulted in an increase in the MR Value. Conversely, when keeping the ultrasound time unchanged, an initial increase in the ChCl/OX ratio led to higher MR Values followed by a subsequent decrease. The correlation between ultrasonic time and DES mass was found to be statistically significant ($p=0.004$).

When maintaining a constant ultrasonic time, an increase in DES mass resulted in a corresponding elevation of the MR Value. Similarly, when keeping the DES mass constant, longer ultrasonic times were associated with higher MR Values.

The equation was solved using Software Design Expert 13, and the optimal extraction conditions were determined as follows: a molar ratio of ChCl to OX at 1:2, a mass of DES at 0.98 g, and an ultrasonic time of 40 min. Under these optimized conditions, the response surface model predicted an MR Value of 9.06.

Analytical performance

Validation parameters including limit of detection (LOD: 3 SD/m, standard deviation of blank obtained from twelve replicates; m, slope of calibration curve), limit of quantification (LOQ: 10 SD/m), linear range (LR) and coefficient of determination (r^2) were obtained separately for each target analytes. All of the calculated data are presented in Table 2.

Table 2

Figures of merit of the proposed method for the target analytes (sample mass 0.1 g, DESs mass 0.98 g, ultrasound 40 min, 1ChCl:2Ox)

Analytes	LOD ^a (mg kg ⁻¹)	LOQ ^b (mg kg ⁻¹)	LR ^c (mg kg ⁻¹)	r^{2d}
K	0.291	0.969	200–4000	0.9996
Na	0.093	0.309	5–200	0.9995
Ca	0.584	1.947	50–4000	0.9998
Mg	0.351	1.170	50–4000	0.9998
Fe	0.144	0.479	5–600	0.9997
Mn	0.037	0.122	5–200	0.9999
Cu	0.115	0.384	2–200	0.9995
Zn	0.140	0.466	5–200	0.9998
P	1.322	4.406	200–4000	0.9996

^a Limit of detection; ^b Limit of quantification; ^c Linear range; ^d Coefficient of determination

The LRs of the calibration curve encompasses the lowest and highest concentrations of the target elements in rice, while seven calibration points are established for each target element, including blank points. As shown in Table 2, the LRs of the calibration curves of the target analytes were in the ranges of 2~200 and 200~4000 mg kg⁻¹ with $r^2 \geq 0.9995$. The LODs and LOQs were in the ranges of 0.037~1.322 and 0.122~4.406 mg kg⁻¹, respectively. The analytical figures of merit of the developed method were comparable to or better than other extraction procedures reported in the literature for the determination of the target analytes.

Validation of the developed method

In order to assess the accuracy of the proposed methodology, Certified reference samples (GSB1,

rice; GSB21, rice) were subjected to digestion using the proposed procedure and subsequent determination of analytes was performed by ICP-OES (Table S2, S3). The average measured value ($n=7$), certified value, relative errors (%RE), and relative standard deviation (%RSD) ($n=7$) for each reference sample were obtained and presented in Table 3.

The relative error (%RE) was employed to evaluate the accuracy of seven replicates for each sample. The reference samples demonstrated a %RE range of -6.6–3.8%. The obtained result closely approximated the reference value, indicating a high degree of accuracy. The precision of each sample was assessed by calculating the relative standard deviation (%RSD) based on seven replicates. As shown in Table 3, the %RSD values for the reference samples were found to be below 5.5%, indicating a high degree of precision.

Table 3

Determination of target analytes in reference samples using the proposed methods (ChCl-OX) by ICP-OES

Sample	Elements	Certified (mg/kg)	Measured (mg/kg)	RE (%)	RSD (%)
GSB1 (Rice)	K	1380±70	1352±42	-2.0	3.1
	Na	25±8	24.5±0.6	-2.6	2.5
	Ca	110±10	111±2.8	1.3	2.5
	Mg	410±60	398±9.3	-3.0	2.3
	Mn	17±1	16.5±0.4	-2.7	2.5
	Fe	7.6±1.9	7.10±0.2	-6.6	2.6
	Cu	4.9±0.3	4.63±0.2	-5.6	4.7
	Zn	23±2	21.7±0.8	-5.5	3.7
	P	1360±60	1297±15	-4.6	1.2
GSB21 (Rice)	K	1300±100	1246±28	-4.2	2.3
	Na	25±2	22.9±0.6	-8.3	2.7
	Ca	110±10	113±4.3	3.0	3.8
	Mg	420±20	406±14	-3.2	3.3
	Mn	10.6±0.6	11.0±0.6	3.8	5.5
	Fe	7.5±2.0	7.3±0.2	-3.2	3.4
	Cu	1.7±0.1	1.67±0.04	-2.0	2.4
	Zn	13.0±0.6	13.3±0.6	2.1	4.4
	P	1270±40	1217±30	-4.2	2.4

Values are for mean±extended uncertainty of seven replicate measurements ($n=7$). Values in parenthesis are reference value

Analytical application in rice samples

The proposed method was utilized to determine the analytical constituents in 14 actual rice samples (9 white and 5 brown rice). The determination of analytical constituents in

rice samples by ICP-OES with microwave digestion- $\text{HNO}_3/\text{H}_2\text{O}_2$ dissolution is widely recognized as a well-established method. Therefore, it was adopted as the reference method for this study (Table S4). The results are presented in Fig. 2.

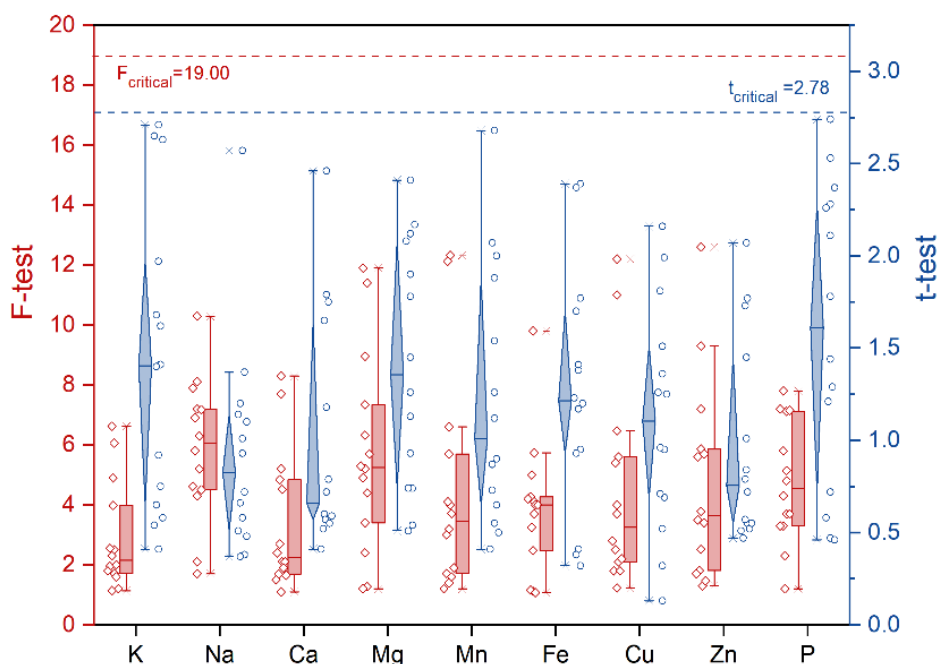


Fig. 2 – Statistical analysis between measured values obtained from the developed and reference methods.

The *F* test was employed to compare the analytical results, using a critical-value of 19.00. Experimental values ≤ 19.00 indicate no statistically significant difference in precision between the two methods at a confidence level of 95%. As depicted in Fig. 2, the calculated *F* values were found to be below the critical value for this test ($F_{\text{critical}}=19.00$). Therefore, it can be concluded that there is no statistically significant difference in precision between the two methods at a confidence level of 95%. The accuracy of the developed procedure was validated using the Student's *t*-test. The paired *t*-values of both methods were found to be below the critical value for this study ($t_{\text{critical}} = 2.78$). These results indicate that there is no statistically significant difference in the content of analytical elements between the established method and the reference method at a 95% confidence level.

METHODOLOGY

Instrument

The quantification of the analytes (K, Na, Ca, Mg, Fe, Mn, Cu, Zn and P) was achieved using an ICP-OES instrument (iCAP 6000, Thermo Scientific) equipped with a charge injection device (CID) detector. The Avanti J-E centrifuge (Beckman Coulter, Germany) and the M5800-J ultrasonic cleaner (Branson, USA) were employed for ultrasound-assisted extraction and centrifugation, respectively. Fourier transform infrared (FTIR) spectra were measured using a Nicollet 510 FTIR spectrometer (Nicollet Instruments, Madison). The operating parameters of ICP-OES are presented in Table 4.

Table 4
Operating parameter of ICP-OES

Item	Parameter
Pump rate (rpm)	50
Nebulizer	Standard concentric
Nebulizer gas flow (L/min)	0.6
Spray chamber	Standard cyclonic
Centre tube (mm)	2.0
RF forward power (W)	1150
Auxiliary flow (L/min)	0.5
Integration time	15 s UV / 10 s Vis
View mode	Radial
Emission line (nm)	K (766.496), Na (589.592), Ca (317.933), Mg (279.079), Fe (238.204), Mn (257.610), Cu (324.754), Zn (206.200), P (177.495)

Reagents, solutions and samples

The solutions were all prepared using high purity water (18.2 M Ω cm resistivity) obtained from the GN-RO-500 Total Water System (Shuangfeng, Beijing, China). Choline chloride (>99%, C₅H₁₄NCIO), ultra-pure nitric acid (65% HNO₃), purified grade oxalic acid (99.999%), and 30% w/w hydrogen peroxide were procured from Sinopharm Chemical Reagent Co., Ltd, China. The calibration process employed standard working solutions, which were prepared by diluting 1000 mg/L multi-element standard solutions (IGGE, China) with 1% HNO₃. The validation experiments were conducted

using the reference samples GSB1 (rice, IGGE, China) and GSB21 (rice, IGGE, China).

Preparation of deep eutectic solvent

The synthesis of DES was conducted following the established protocol outlined in previous studies.^{13,22} The different types of deep eutectic solvents (DESS) were synthesized by combining choline chloride (ChCl) and oxalic acid (OX) in molar ratios of 1:1, 1:1.75, and 1:2.5. Precise amounts of ChCl and OX were introduced into a 50-mL round-bottom flask, which was then heated to a temperature of 60 °C using a magnetic stirrer

heating plate. The mixture was continuously stirred with a magnetic stirrer bar until a homogeneous, colorless liquid was formed.

Optimization of sample digestion

The optimum conditions for sample digestion were determined using a Box-Behnken design, as shown in Table 1. The experimental design consisted of 17 experiments, including 5 replicates at the central point. To assess the effectiveness of each digestion procedure, recoveries of the analytes were compared.

The plant sample (100 mg) was placed into a 10 mL polypropylene vessel, followed by the addition of varying amounts (0.1, 0.55, 1 g) of DESs (choline chloride and oxalic acid in molar ratios of 1:1, 1:1.75, and 2.5). The vessels were subjected to ultrasonic treatment for different durations (10, 25, and 40 minutes) in an ultrasonic bath. Subsequently, the vessels were transferred onto a digester and maintained at a temperature of 80 °C for a duration of 10 minutes. After completion of the extraction process, the vessel was allowed to cool down to ambient temperature. The resulting solution underwent centrifugation at 4000 rpm for a duration of 10 minutes to separate the liquid and solid residues. The supernatant phase obtained was diluted with ultra-pure water up to a final volume of 25 mL before being analyzed using ICP-OES. Additionally, blanks were prepared alongside each batch of samples. A mathematical tool based on Eq. 2³⁸ was utilized to employ multiple responses (MR) in the design for quantified elements.

$$\text{MR} = \left(\frac{R_{I1}}{R_{\max I1}} \right) + \left(\frac{R_{I2}}{R_{\max I2}} \right) + \left(\frac{R_{I3}}{R_{\max I3}} \right) + \dots + \left(\frac{R_{In}}{R_{\max In}} \right) \quad (2)$$

where R_{In} is the recovery of each analyte in the experiment and $R_{\max In}$ is the maximum recovery of the analyte in the design.

Conventional acid digestion

The digestion vessel with a capacity of 70 mL was hermetically sealed after introducing 100 mg of plant sample, 5.0 mL of ultrapure HNO₃, and 1.0 mL of H₂O₂. The sealed vessel was stored for 2 hours. The microwave digestion program consisted of the following steps: (I) ramping up to 180 °C over a period of 5 min, (II) maintaining at 180 °C for

15 min, and (III) cooling down to 60 °C within a span of 15 min. After digestion, the mixture was transferred to a polyethylene colorimetric tube with a volume of 25 mL and diluted with ultra-pure water to reach a final volume of 25 mL. The resulting extracts were determined by ICP-OES, and an additional blank sample was included for analysis.

CONCLUSIONS

A rapid, accurate, efficient and environmentally friendly method for the analysis of K, Na, Ca, Mg, Fe, Mn, Cu, Zn and P in rice samples was developed based on ultrasound-assisted extraction. The synthesis of deep eutectic solvents (DESs) based on choline chloride and oxalic acid has yielded a promising environmentally friendly solvent for elemental analysis. The optimal reaction conditions for extracting target analytes were determined by optimizing the key parameters based on a Box-Behn design. The method validation successfully demonstrated the application of this developed methodology for extracting target analytes from rice samples with diverse compositions. The accuracy of this method did not exhibit a significant difference when compared to the microwave digestion technique. The developed method can be considered a favorable alternative to the conventional approach, given its capacity to bypass the requirement for large quantities of acid. Moreover, this technique offers several advantages, including simplicity, rapid extraction time, cost-effectiveness, and environmental compatibility.

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