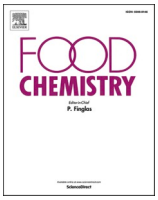
Food Chemistry 439 (2024) 138140

Contents lists available at ScienceDirect

Food Chemistry

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



Analytical Methods

Determination of copper in rose tea samples using flame atomic absorption spectrometry after emulsification liquid–liquid microextraction

Bedrihan Kartoğlu [a], Süleyman Bodur [a,b,c], Damla Zeydanlı [d], Tuğçe Göver [e], Ecem Özaydın [a], Emine Gülhan Bakırdere [f], Sezgin Bakırdere [a,g,*]

[a] Yıldız Technical University, Faculty of Art and Science, Department of Chemistry, 34220 İstanbul, Türkiye
[b] İstinye University, Faculty of Pharmacy, Department of Analytical Chemistry, 34010 İstanbul, Türkiye
[c] İstinye University, Scientific and Technological Research Application and Research Center, 34010 İstanbul, Türkiye
[d] Gelişim University, Vocational School of Health Care Services, Department of Laboratory Technology, 34310, İstanbul, Türkiye
[e] Selçuk University, Faculty of Pharmacy, Department of Analytical Chemistry, 42130, Konya, Türkiye
[f] Yıldız Technical University, Faculty of Education, Department of Mathematics and Science Education, 34349 İstanbul, Türkiye
[g] Turkish Academy of Sciences (TÜBA), Vedat Dalokay Street, No: 112, Çankaya, 06670 Ankara, Türkiye

ARTICLE INFO

Keywords:
Copper
Emulsification liquid–liquid microextraction
Flame atomic absorption spectrometry
Rose tea
Matrix matching calibration

ABSTRACT

Rose tea infusion has gained popularity worldwide due to its health benefits. However, it is known that tea plants can be contaminated with heavy metals including copper. Hence, an accurate and applicable analytical method namely emulsification liquid–liquid microextraction based deep eutectic solvent – flame atomic absorption spectrometry (ELLME-DES-FAAS) was proposed to determine copper at trace levels in rose tea samples. Under the optimum experimental conditions, analytical figures of merit for the developed method were examined, and dynamic range, limit of detection (LOD) and limit of quantification (LOQ) were found to be 5.07–246.61 μg/kg (mass-based) with 0.9992 coefficient of determination, 2.50 μg/kg and 8.32 μg/kg, respectively. A matrix matching calibration strategy was employed to boost recovery results, and the acceptable recovery results were recorded between 95.9 % and 118.4 %. According to recovery results, the developed analytical method can be safely employed to determine the concentration of copper in rose tea samples accurately.

1. Introduction

Copper is an essential trace metal for living organisms (De Luca, Barile, Arciello, & Rossi, 2019), but excess dietary intake of copper is associated with risks to human health (Krstić, Urošević, & Pešovski, 2018; Shabbir, Sardar, Shabbir, Abbas, Shamshad, Khalid, & Shahid, 2020). All around the world, rose tea infusion has become a popular beverage in terms of a wide variety of health benefits such as analgesic, inflammatory, antiviral, antifungal, antioxidant, and antibacterial (Bian et al., 2023). On the other hand, the accumulation of heavy metals such as copper and lead can occur in tea plants during their growth processes (Qin & Chen, 2007). For these reasons, an applicable and accurate analytical method is required to qualitatively and quantitatively determine copper in tea samples for the evaluation of negative and positive health effects for humans.

In literature, there are several spectroscopic (Tobiasz & Walas, 2014) and electroanalytic (Almeida, Richter, & Munoz, 2014; Wang, Dai, Wang, Ma, & Lin, 2017) instrumentation methods to determine copper in various matrices. Although flame atomic absorption spectrometry (FAAS) systems have relatively low operational costs and are easy to use, these systems possess low sensitivity because of the pneumatic nebulization as Achilles' Heel (Browner & Boorn, 1984). Additionally, electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma–mass spectrometry (ICP-MS) provide higher sensitivity than other atomic spectroscopic methods but they have some limitations arising from the matrices. For these reasons, extraction and preconcentration protocols have been used to eliminate these problems (Pereira & Arruda, 2003). Additionally, FAAS systems have been generally combined with microextraction methods to reach lower detection limits (Arpa, Albayati, & Yahya, 2018; Şahin & Tokgöz, 2010; Seidi & Alavi, 2019; Shrivas & Jaiswal, 2013; Trindade et al., 2021).

In almost every analytical process, sample(s) is treated with a proper sample preparation method to make a suitable sample form for the related instrument despite the fact that sophisticated analytical

* Corresponding author.
E-mail address: bsezgin@yildiz.edu.tr (S. Bakırdere).

https://doi.org/10.1016/j.foodchem.2023.138140
Received 5 October 2023; Received in revised form 30 November 2023; Accepted 2 December 2023
Available online 4 December 2023

instruments have been developed for the determination of inorganic analyte(s) (Shishov, Bulatov, Locatelli, Carradori, & Andruch, 2017). New analytical procedures developed should provide the requirements for green chemistry to reduce the risk of used chemicals for humankind and the environment (Keith, Gron, & Young, 2007). In analytical chemistry, deep eutectic solvents (DESs), which are a suitable solvent for the green chemistry concept, have been utilized as alternative solvents in liquid phase microextraction instead of toxic organic solvents (Santana-Mayor, Rodríguez-Ramos, Herrera-Herrera, Socas-Rodríguez, & Rodríguez-Delgado, 2021). Nowadays, DESs based liquid phase extraction/microextraction methods are one of the top topics in analytical chemistry to attain a proper sample form prior to the related analytical measurement in addition to the extraction and preconcentration of target analyte from various matrices. Khezeli and co-workers firstly reported emulsification liquid–liquid microextraction based DES (ELLME-DES) to extract/preconcentrate organic analytes from water samples prior to high performance liquid chromatography – UV detection (HPLC-UV). In the ELLME-DES process, a hydrogen bond donor (phenol) and a hydrogen bond acceptor (choline chloride) were used to produce a deep eutectic solvent utilized as a water-miscible extraction solvent. After the addition of DES produced, an aprotic solvent (tetrahydrofuran (THF)) as an emulsifier agent was added to the homogenous solution to aggregate the DES molecule in order to obtain phase separation (Khezeli, Daneshfar, & Sahraei, 2015; Ramezani, Ahmadi, & Yamini, 2022). In addition, various DES compositions have been employed in the preconcentration and separation of inorganic analyte(s) from various matrices for the determination of analyte(s) at trace levels (Shishov et al., 2017).

The main purpose of this study was to develop a green, efficient and accurate analytical method in order to quantify copper in rose tea samples by FAAS. A lab-synthesized ligand, DES (choline chloride: phenol (1:2)) and THF were used as a complexation agent, a water-miscible extraction solvent and an emulsification agent, respectively. The developed extraction/preconcentration method was implemented to rose tea samples in order to make evaluation in terms of the applicability and accuracy. To the best of our knowledge, this is the first study for the quantitative determination of copper at trace levels in rose tea samples by ELLME-DES-FAAS method.

2. Materials and methods

2.1. Chemicals and reagents

2-hydroxy-1-naphthaldehyde (purity $\geq$ 97.5 %) and 2-aminophenol (purity $\geq$ 98.5 %) were bought from Alfa Aesar (Haverhill, USA). Tetrahydrofuran (purity $\geq$ 99.9 %), choline chloride (purity $\geq$ 98 %), phenol (purity $\geq$ 99.5 %) and p-toluenesulfonic acid (purity $\geq$ 98.5 %) were purchased from Sigma-Aldrich (Darmstadt, Germany) while copper standard solution (1000 $\pm$ 2 mg/L) and ethanol (purity $\geq$ 98 %) were supplied from Merck (Darmstadt, Germany). Elga PureLab Flex 3 (High Wycombe, England) system was utilized to produce ultrapure water (resistivity 18.2 MΩ.cm) that was used in all cleaning process and the preparation of standard solutions.

2.2. Instrumentation

A flame atomic absorption spectrometry (FAAS, ATI UNICAM 929 AA, UNICAM, England), which equipped with a burner head, a copper hollow cathode lamp (3.3 mA working current, 0.50 nm spectral bandwidth and 324.8 nm analytical line) and a deuterium lamp, was used to qualify and quantify the analyte. An acetylene/air mixture was employed to produce a stoichiometric flame for the atomization process. The outlet pressure of acetylene and air was set at 1.0 and 5.0 bar with the help of pressure gauges, respectively.

2.3. Synthesis of complexation agent

The complexation agent was synthesized according to previous report published by our research laboratory (Tışlı, Gösterişli, Zaman, Bakırdere, & Bakırdere, 2020). 2-hydroxy-1-naphthaldehyde (10 mmol, 1.72 g) was dissolved in 20 mL of ethanol and this solution was transferred to the three-necked flask. The temperature of solution was set at 60 °C with the help of magnetic stirrer having temperature control after the addition of p-toluenesulfonic acid monohydrate (0.01 g) as catalyst. Then, 20 mL of 2-amino phenol (5 mmol, 0.55 g) prepared in ethanol was added to the reaction mixture drop by drop. The reaction was continued at 60 °C by applying reflux for three hours. In the result of this reaction, an orange precipitate was observed. After the cooling process to room temperature, the precipitate was filtered and then washed with ethanol to remove any impurities. The product was held in a drying oven at 60 °C for one day to remove residual solvent.

2.4. Synthesis of deep eutectic solvent

Phenol and choline chloride were used as hydrogen bond donor and hydrogen bond acceptor to form a water-miscible extraction solvent, respectively. DESs with four different molar ratios (choline chloride: phenol, 1:1, 1:2, 1:3, and 1:4) were synthesized. During the synthesis of DESs, the proper amounts of choline chloride and phenol were weighed in the same tube, and vortex mixing was applied for approximately 10 min to complete the synthesis. After the synthesis was completed, the solutions possessing different viscosities were obtained. In addition, it was observed that the viscosity of solution decreased when the amount of phenol increased.

2.5. Emulsification liquid–liquid microextraction based deep eutectic solvent procedure

In the extraction/preconcentration step, 0.50 mL of pH 4 buffer solution was added to 8.0 mL aqueous solution and then complexation agent (1.25 mL, 0.01 % (*w/v*)) was pipetted into the solution. After, 15 s vortex mixing was applied to the solution in order to obtain a homogeneous solution. The synthesized DES solution (0.40 mL, choline chloride:phenol (1:2 M ratio)) was added onto the solution and then the solution was vortexed for 15 s. After the addition of DES solution, 1.0 mL of emulsification agent (THF) was added to the solution, and it was observed that a cloudy solution was formed. The vortex process was implemented for 30 s to the solution in order to enhance the interaction between the extraction solvent and the analyte. After the vortex process, the solution was centrifuged for 2.0 min to obtain phase separation efficiently. Finally, approximately 150 μL of upper phase was transferred into a clean centrifuge tube and then the phase was directly introduced to the FAAS system for its analysis.

2.6. Samples

Rose bud samples (two different brands), which are used to make tea, were purchased from the local market in İstanbul, Türkiye. Each rose bud sample (2.2 g) was weighed in two separate volumetric flasks (200 mL), and then the samples were completed to 200 mL with drinking water. After, the samples were brewed as made at home, and then 30.0 g of brewed samples were put into two separate clean polypropylene bottles after cooling at room temperature. After that, the samples were filled to 300 g with ultrapure water. For the matrix matching calibration strategy, the proper amounts of copper aqueous solutions were weighed into the polypropylene bottles and then completed to 40.0 g with the prepared sample solutions. After the spiking procedure, 8.0 mL of the spiked sample solutions for each concentration level was pipetted to three separate centrifuge tubes to perform the developed extraction/preconcentration method.

2.7. The application of statistical test for data analysis

A post hoc comparison-based statistical test with analysis of variance (ANOVA) evaluates the significant difference between the variables (King, 2010). For the assessment of difference in pair comparisons, Tukey's honestly significant difference (HSD) statistical test has been employed (Brown, 2005). During the evaluation of optimization parameters, Tukey's post hoc test was applied to the mean values of the tested variables using Jeffry's Amazing Statistics Program (JASP, 0.18.1 version). While the different lower-case letters (a, b or c) show significant statistical differences between the variables, the same lower-case letters present non-significant statistical differences.

3. Results and discussion

3.1. The effects of buffer solution pH and volume

It is known that the pH of sample solution affects the reaction kinetics and the stability of formed complex(s) (Duda, 2002). Therefore, the effect of buffer solution pH was examined to enhance the signal to noise ratio belonging to the analyte. For this purpose, eight different pH buffer solutions (between 3 and 10) were tried. In the result of this optimization, pH 4 buffer solution was selected as optimum condition although approximately the same analytical signals were obtained from pH 4 and pH 10 buffer solutions (Fig. 1A) because copper could precipitate as its hydroxides at basic pH levels.

After pH optimization, six different volumes of buffer solution were tested to determine the optimum buffer volume. All buffer volumes except 1.50 mL provided almost the same analytical signals. Furthermore, 1.50 mL of buffer solution supplied the highest analytical signals but it caused to form a low amount of organic phase, and hence it was difficult to take the organic phase at 1.50 mL of buffer solution. For this reason, 0.50 mL of buffer solution was determined as the optimum volume to keep the buffer capacity high in real samples. As can be seen in Fig. 1(B), no statistically significant differences were observed between all tested variables according to Tukey's post hoc test.

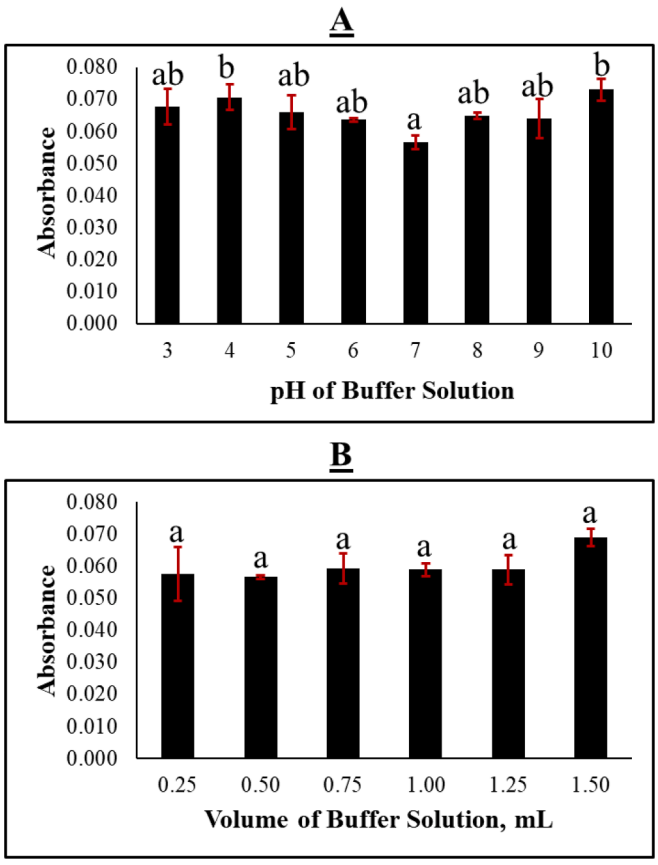


Fig. 1. The effects of buffer solution pH (A) and volume (B). Lower-case letters show the significant differences between the variables for n = 3 ($p < 0.05$ at 95 % confidence interval).

3.2. The effects of complexation agent concentration and volume

The concentrations of complexation agent varied in the range of 0.005–0.05 % (*w/v*) were compared to each other in order to increase complex output. As can be seen in Figure S1(A), similar analytical signals were obtained from all tested complexation agent concentrations. This result shows that the reaction efficiency between the analyte ions and the complexation agent is high. The concentration of complexation agent (0.01 % (*w/v*) was used in further studies. In addition, the volume of complexation agent was optimized to enhance the signal output. It was observed that the volume of formed organic phase lowered while the volume of added complexation agent increased, and also it was difficult to separate the organic phase at 1.75 mL. Hereby, 1.25 mL of complexation agent was chosen as the optimum volume. Additionally, the volume of complexation agent affected the organic phase formation due to ethanol content in the complexation agent, therefore; a linear increment (Figure S1B) in the absorbances was observed in this optimization step.

3.3. The effects of molar ratio and volume of deep eutectic solvent

The molar ratios of hydrogen bond donor and acceptor chemicals affect the physical properties such as conductivity, melting point, density and viscosity for the formed deep eutectic solvents (Guo, Hou, Ren, Tian, & Wu, 2013). Therefore, the molar ratio of choline chloride and phenol was important to increase the extraction efficiency in the developed procedure. Four different choline chloride:phenol (1:1, 1:2, 1:3 and 1:4) were tested to evaluate the effects on the analyte signal. While there was no phase separation at choline chloride:phenol (1:1), a linear decrement was observed on the analytical signals from 1:2 to 1:4 M ratios (Fig. 2A). The increment of phenol amount in the formed deep eutectic solvent caused high volume phase separation, hence; choline chloride:phenol (1:2) provided the highest analytical signals due to the preconcentration factor. Further optimizations were carried out with 1:2 M ratio of choline chloride:phenol.

It is known that there is an inverse relationship between the extraction solvent volume and the preconcentration/enrichment factor (Alshana, Hassan, Al-Nidawi, Yilmaz, & Soylak, 2020; Cantwell & Losier, 2002). For this reason, 0.30, 0.40, 0.50, 0.75 and 1.0 mL of DES were used to extract/preconcentrate the analyte from aqueous solutions. There was no observable phase separation for 0.30 mL of DES and the highest analytical signals were recorded for 0.40 mL of DES (Fig. 2, B). In addition, 0.40 mL of DES volume provided statistically different results compared to other tested volumes. Hence, this volume was selected as the optimum one.

3.4. The effect of emulsification agent

THF was employed as an emulsification agent to separate the DES molecule in the developed extraction protocol·THF volume directly affected obtaining settled extraction phase volume and the analytical signals reduced while increasing the volume of THF (Figure S2). In spite of obtaining the highest absorbances from 0.75 mL, it was difficult to collect the formed phase. For this reason, 1.0 mL of THF volume was chosen as the optimum one for further studies.

3.5. The effect of vortex period

A mixing process can augment the extraction efficiency by increasing

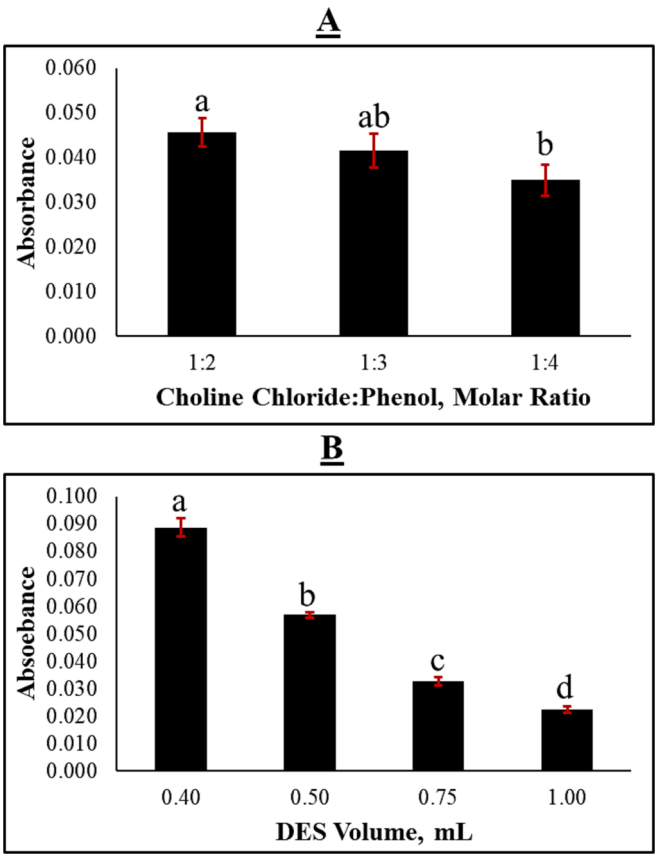


Fig. 2. The effects of DES molar ratio (A) and volume (B). Lower-case letters show the significant differences between the variables for n = 3 ($p < 0.05$ at 95 % confidence interval).

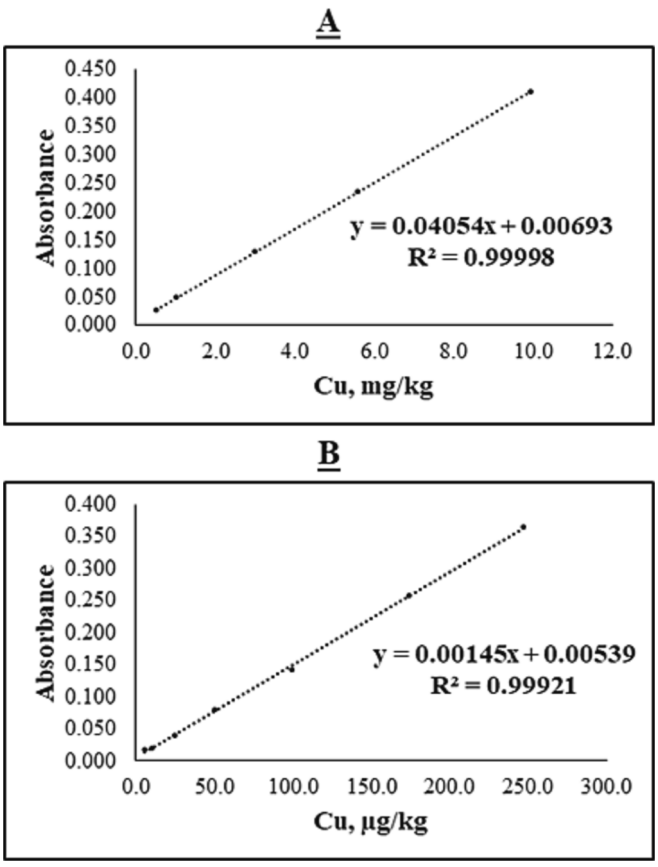


Fig. 3. Calibration plots obtained from the FAAS (A) and the ELLME-DES-FAAS (B) systems.

the interaction between the analyte and extraction solvent. Therefore, vortex mixing was applied to the standard solutions because vortex is an easy, simple and effective apparatus. Four different vortex periods were implemented to the standard solutions and then the solutions applied to vortex mixing were compared to the standard solutions without any mixing process. As can be seen in Figure S3, the highest absorbances were obtained from 30 s which was determined as the optimum value.

3.6. Analytical figures of merit

Under the optimum FAAS conditions, system analytical performance studies were performed to evaluate the dynamic range, coefficient of determination (R^2), limit of detection (LOD) and limit of quantification (LOQ). For this purpose, the copper aqueous standard solutions prepared in the range of 0.26–25.04 mg/kg (seven different concentration) were directly sent to the FAAS system. Dynamic range was determined between 0.49 and 9.96 mg/kg with 0.9999 R^2 while LOD and LOQ values were calculated as 0.12 mg/kg and 0.41 mg/kg, respectively.

For the evaluation of system analytical performance of the developed ELLME-DES-FAAS method, nine different mass-based prepared standard aqueous solutions (5.07 µg/kg–1.02 mg/kg) were introduced to the FAAS system after applying the developed ELLME-DES method. Dynamic range, R^2, LOD and LOQ for the developed method were recorded as 5.07–246.61 µg/kg, 0.9992, 2.50 µg/kg and 8.32 µg/kg, respectively. When the proposed ELLME-DES-FAAS method was compared to the FAAS method in terms of the enhancement in detection power (EDP) and calibration sensitivity (ECS), EDP and ECS values were found to be 48.7 and 35.8 folds, respectively. Calibration plots obtained from the FAAS and the ELLME-DES-FAAS systems are given in Fig. 3. LOD, LOQ, EDP and ECS values were calculated using the formulas given below.

$$LOD = 3 \bullet \frac{S.D.}{m} \quad (1)$$

$$LOD = 10 \bullet \frac{S.D.}{m} \quad (2)$$

$$EDP = \frac{LOD_{FAAS}}{LOD_{ELLME-DES-FAAS}} \quad (3)$$

$$ECS = \frac{m_{ELLME-DES-FAAS}}{m_{FAAS}} \quad (4)$$

S.D.: Standard deviation (n = 6) of the lowest concentration in calibration plot.
m: Slope of calibration plot.
LOD_x: LOD value of x (x: FAAS or ELLME-DES-FAAS).
m_x: Slope of calibration plot belonging to x (x: FAAS or ELLME-DES-FAAS, the concentration units must be the same in both calibration plots).

In Table 1, the system analytical performance values are summarized and also the developed method was compared to literature findings in terms of the analytical figures of merit.

It is clear that the developed method is superior according to literature findings in terms of dynamic range and LOD/LOQ values (Table 1). Some literature findings found in Table 1 have tedious experimental steps and more sample preparation periods. However, the proposed method possesses a low sample preparation period and easy treatment steps. Furthermore, the developed ELLME-DES method can be combined with more sensitive instrumental methods such as GFAAS and ICP-MS systems to obtain lower detection limits.

Table 1
Analytical figures of merit for the developed ELLME-DES-FAAS method and the literature comparison.

Method	Dynamic Range	LOD[a]	LOQ[b]	Coefficient of Determination (R^2)	EDP/ECS[c]	Reference
FAAS[d]	0.49–9.96 mg/kg	121.6 μg/kg	405.3 μg/kg	0.9999	49/36	This study
ELLME-DES-FAAS[e]	5.07–246.61 μg/kg	2.50 μg/kg	8.32 μg/kg	0.9992		
EA-DES-DLLME-FAAS[f]	10.0–100 μg/L	2.9 μg/L	9.7 μg/L	–	–	(Arpa et al., 2018)
DLLME-FAAS[g]	25–100 μg/L	6.3 μg/L	19 μg/L	–	–	(Seeger et al., 2015)
HF-LPME-FAAS[h]	10–15000 μg/L	4.0 μg/L	–	0.9952	–	(Es'haghi & Azmoodeh, 2010)
SA-PT-DSPE-FAAS[i]	0.025–0.50 mg/L	8.0 μg/L	26.6 μg/L	0.9977	20.6 (EDP)	(Demir, Öner, Bodur, Er, & Bakırdere, 2021)
SA-PT-DSPE-SQT-FAAS[j]	0.010–0.25 mg/L	3.7 μg/L	12.5 μg/L	0.9993	44.0 (EDP)	
SFODME-FI-FAAS[k]	1.0–25.0 μg/L	0.4 μg/L	1.1 μg/L	–	–	(Şahin & Tokgöz, 2010)

[a] LOD: Limit of detection.
[b] LOQ: Limit of quantification.
[c] EDP/ECS: The enhancement in detection power and the enhancement in calibration sensitivity.
[d] FAAS: Flame atomic absorption spectrometry.
[e] ELLME-DES-FAAS: Emulsification liquid–liquid microextraction based deep eutectic solvent – flame atomic absorption spectrometry.
[f] EA-DES-DLLME-FAAS: Effervescence-assisted dispersive liquid–liquid microextraction based deep eutectic solvent – flame atomic absorption spectrometry.
[g] DLLME-FAAS: Dispersive liquid–liquid microextraction – flame atomic absorption spectrometry.
[h] HF-LPME-FAAS: Hollow fiber supported liquid membrane microextraction – flame atomic absorption spectrometry.
[i] SA-PT-DSPE-FAAS: Syringe assisted pipette tip dispersive solid phase extraction – flame atomic absorption spectrometry.
[j] SA-PT-DSPE-SQT-FAAS: Syringe assisted pipette tip dispersive solid phase extraction – slotted quartz tube – flame atomic absorption spectrometry.
[k] SFODME-FI-FAAS: Solidified floating organic drop microextraction – flow injection flame atomic absorption spectrometry.

3.7. Real sample analysis and spiking experiments

Two rose tea samples (preparation steps were detailed in *Section 2.6*) were directly sent to the FAAS system after the treatment with the developed microextraction method. After the analysis of samples, the analyte was not detected in the samples. Hence, spiking experiments were performed to test the applicability and accuracy of proposed method. For this purpose, the proper amounts of copper aqueous solution were spiked to two tea matrices detailed in *Section 2.6*. Under the optimum FAAS and ELLME-DES conditions, the solutions were analyzed and recovery results for both matrices were recorded between 66.4 and 74.4 % via external calibration strategy. It is clear that there were matrix effects on the analyte, therefore; matrix matching calibration strategy was used to enhance recovery results. After the application of matrix matching calibration strategy, recovery results for Brand A and B rose tea samples were calculated in the range of 96.0–104.5 % and 95.9–118.4 %, respectively. The spiked experimental concentration of analyte for Brand A sample was calculated via the constructed calibration plot obtained from Brand B (4 different concentrations) and vice versa for Brand B (the calibration plot belonging to Brand A was constructed with 5 different concentrations). All recovery results obtained from external calibration and matrix matching calibration strategies are summarized in Table 2.

4. Conclusion

An easy and green ELLME-DES method was developed to enhance the detection power of FAAS system for the determination of copper at trace levels in rose tea samples. A Schiff base ligand was synthesized in our laboratory to form a copper complex for the extraction/preconcentration of analyte from rose tea samples. The optimization studies were completed using univariate optimization approach to increase the signal to noise ratio belonging to the analyte in addition to preconcentration/enrichment factor. After the optimizations, system analytical performance studies were performed and LOD/LOQ values for the ELLME-DES-FAAS method were recorded as 2.50/8.32 μg/kg. Spiking experiments were carried out for the evaluation of accuracy and applicability of proposed method. The acceptable recovery results (95.9–118.4 %) were obtained via matrix matching calibration strategy while external calibration strategy led to low recovery results due to negative matrix effects. The proposed method can be used to accurately and precisely determine copper in rose tea samples using matrix matching calibration strategy.

Table 2
Recovery results for copper in the spiked rose tea samples.

Brand	Spiked Concentration, μg/kg	External Calibration		Matrix Matching Calibration	
		% Recovery	±SD *	% Recovery	±SD *
A	50.02	66.4	4.2	96.0	8.8
	76.31	72.3	4.8	101.0	6.8
	99.33	69.0	8.5	96.5	12.0
	172.72	74.4	3.7	104.5	5.2
B	26.51	69.5	3.1	118.4	3.5
	50.05	73.6	2.8	110.7	5.2
	101.37	72.0	1.2	100.2	1.5
	117.74	71.0	3.4	95.9	4.4

* Uncertainties (±): Standard deviation for triplicate measurements.

Ethical approval

This article does not contain any studies with human participants or animals.

Funding

Not applicable.
Performed by any of the authors.
Code availability:
Not applicable.
Informed consent:
Not applicable.

CRediT authorship contribution statement

Bedrihan Kartoğlu: Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. **Süleyman Bodur:** Data curation, Formal analysis, Validation, Visualization, Writing – original draft. **Damla Zeydanlı:** Formal analysis, Validation, Visualization, Writing – original draft. **Tuğçe Göver:** Formal analysis, Validation, Visualization, Writing – original draft. **Ecem Özaydın:** Formal analysis, Validation, Visualization, Writing – original draft. **Emine Gülhan Bakırdere:** Formal analysis, Validation, Writing – original draft. **Sezgin Bakırdere:** Conceptualization, Investigation, Methodology, Supervision, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

The authors dedicated this publication to the 100th anniversary of the Republic of Türkiye. As scientists raised by Türkiye, they are proud to be citizens of this country.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2023.138140.

References

Almeida, E. S., Richter, E. M., & Munoz, R. A. A. (2014). On-site fuel electroanalysis: Determination of lead, copper and mercury in fuel bioethanol by anodic stripping voltammetry using screen-printed gold electrodes. *Analytica Chimica Acta, 837*, 38–43. https://doi.org/10.1016/j.aca.2014.05.031

Alshana, U., Hassan, M., Al-Nidawi, M., Yilmaz, E., & Soylak, M. (2020). Switchable-hydrophilicity solvent liquid-liquid microextraction. *TrAC - Trends in Analytical Chemistry, 131*, Article 116025. https://doi.org/10.1016/j.trac.2020.116025

Arpa, Ç., Albayati, S., & Yahya, M. (2018). Effervescence-assisted dispersive liquid-liquid microextraction based on deep eutectic solvent for preconcentration and FAAS determination of copper in aqueous samples. *International Journal of Environmental Analytical Chemistry, 98*(10), 938–953. https://doi.org/10.1080/03067319.2018.1517872

Bian, Y., Feng, Y., Zhang, A., Qi, X., Ma, X., Pan, J., … Liang, L. (2023). Residue behaviors, processing factors and transfer rates of pesticides and metabolites in rose from cultivation to consumption. *Journal of Hazardous Materials, 442*, Article 130104. https://doi.org/10.1016/j.jhazmat.2022.130104

Brown, A. M. (2005). A new software for carrying out one-way ANOVA post hoc tests. *Computer Methods and Programs in Biomedicine, 79*(1), 89–95. https://doi.org/10.1016/j.cmpb.2005.02.007

Browner, R. F., & Boorn, A. W. (1984). Sample Introduction: The Achilles' heel of atomic spectroscopy? *Analytical Chemistry, 56*(7), 786A–A798. https://doi.org/10.1021/ac00271a718

Cantwell, F. F., & Losier, M. (2002). Liquid-liquid extraction. *Comprehensive Analytical Chemistry, 37*, 297–340. https://doi.org/10.1016/S0166-526X(02)80048-4

De Luca, A., Barile, A., Arciello, M., & Rossi, L. (2019). *Copper homeostasis as target of both consolidated and innovative strategies of anti-tumor therapy* (Vol. 55,, 204–213. https://doi.org/10.1016/j.jtemb.2019.06.008

Demir, C., Öner, M., Bodur, S., Er, E.Ö., & Bakırdere, S. (2021). A Simple and efficient extraction method for the preconcentration of copper in tap water and linden tea samples prior to FAAS measurement. *ChemistrySelect, 6*(12), 2906–2912. https://doi.org/10.1002/slct.202100149

Duda, L. L. (2002). Kinetics of the dissolution of copper in aqueous alkaline 2,2′-dipyridyl solutions. *Corrosion Science, 44*(5), 989–995. https://doi.org/10.1016/S0010-938X(01)00128-7

Es'haghi, Z., & Azmoodeh, R. (2010). Hollow fiber supported liquid membrane microextraction of Cu2+ followed by flame atomic absorption spectroscopy determination. *Arabian Journal of Chemistry, 3*(1), 21–26. https://doi.org/10.1016/j.arabjc.2009.12.004

Guo, W., Hou, Y., Ren, S., Tian, S., & Wu, W. (2013). Formation of deep eutectic solvents by phenols and choline chloride and their physical properties. *Journal of Chemical and Engineering Data, 58*(4), 866–872. https://doi.org/10.1021/je300997v

Keith, L. H., Gron, L. U., & Young, J. L. (2007). Green analytical methodologies. *Chemical Reviews, 107*(6), 2695–2708. https://doi.org/10.1021/cr068359e

Khezeli, T., Daneshfar, A., & Sahraei, R. (2015). Emulsification liquid–liquid microextraction based on deep eutectic solvent: An extraction method for the determination of benzene, toluene, ethylbenzene and seven polycyclic aromatic hydrocarbons from water samples. *Journal of Chromatography A, 1425*, 25–33. https://doi.org/10.1016/j.chroma.2015.11.007

King, B. M. (2010). Analysis of variance. In *International Encyclopedia of Education* (pp. 32–36). Elsevier Ltd.. doi: 10.1016/B978-0-08-044894-7.01306-3.

Krstić, V., Urošević, T., & Pešovski, B. (2018). A review on adsorbents for treatment of water and wastewaters containing copper ions. In *Chemical Engineering Science* (Vol. 192, pp. 273–287). Elsevier Ltd. Doi: 10.1016/j.ces.2018.07.022.

Pereira, M. de G., & Arruda, M. A. Z. (2003). Trends in preconcentration procedures for metal determination using atomic spectrometry techniques. *Mikrochimica Acta, 141*(3–4), 115–131. https://doi.org/10.1007/s00604-002-0941-5

Qin, F., & Chen, W. (2007). Lead and copper levels in tea samples marketed in Beijing, China. *Bulletin of Environmental Contamination and Toxicology, 79*(3), 247–250. https://doi.org/10.1007/s00128-007-9008-y

Ramezani, A. M., Ahmadi, R., & Yamini, Y. (2022). Homogeneous liquid-liquid microextraction based on deep eutectic solvents. *TrAC - Trends in Analytical Chemistry, 149*, Article 116566. https://doi.org/10.1016/j.trac.2022.116566

Şahin, Ç. A., & Tokgöz, I. (2010). A novel solidified floating organic drop microextraction method for preconcentration and determination of copper ions by flow injection flame atomic absorption spectrometry. *Analytica Chimica Acta, 667*(1–2), 83–87. https://doi.org/10.1016/j.aca.2010.04.012

Santana-Mayor, Á., Rodríguez-Ramos, R., Herrera-Herrera, A. V., Socas-Rodríguez, B., & Rodríguez-Delgado, M.Á. (2021). Deep eutectic solvents. The new generation of green solvents in analytical chemistry. *TrAC - Trends in Analytical Chemistry, 134*, Article 116108. https://doi.org/10.1016/j.trac.2020.116108

Seeger, T. S., Rosa, F. C., Bizzi, C. A., Dressler, V. L., Flores, E. M. M., & Duarte, F. A. (2015). Feasibility of dispersive liquid-liquid microextraction for extraction and preconcentration of Cu and Fe in red and white wine and determination by flame atomic absorption spectrometry. *Spectrochimica Acta - Part B Atomic Spectroscopy, 105*, 136–140. https://doi.org/10.1016/j.sab.2014.11.002

Seidi, S., & Alavi, L. (2019). Novel and Rapid Deep Eutectic Solvent (DES) Homogeneous Liquid-Liquid Microextraction (HLLME) with Flame Atomic Absorption Spectrometry (FAAS) detection for the determination of copper in vegetables. *Analytical Letters, 52*(13), 2092–2106. https://doi.org/10.1080/00032719.2019.1598425

Shabbir, Z., Sardar, A., Shabbir, A., Abbas, G., Shamshad, S., Khalid, S., … Shahid, M. (2020). Copper uptake, essentiality, toxicity, detoxification and risk assessment in soil-plant environment. In *Chemosphere* (Vol. 259, p. 127436). Elsevier Ltd. Doi: 10.1016/j.chemosphere.2020.127436.

Shishov, A., Bulatov, A., Locatelli, M., Carradori, S., & Andruch, V. (2017). Application of deep eutectic solvents in analytical chemistry. A review. *Microchemical Journal, 135*, 33–38. https://doi.org/10.1016/j.microc.2017.07.015

Shrivas, K., & Jaiswal, N. K. (2013). Dispersive liquid-liquid microextraction for the determination of copper in cereals and vegetable food samples using flame atomic absorption spectrometry. *Food Chemistry, 141*(3), 2263–2268. https://doi.org/10.1016/j.foodchem.2013.04.067

Tışlı, B., Gösterişli, T. U., Zaman, B. T., Bakırdere, E. G., & Bakırdere, S. (2020). Determination of manganese in coffee and wastewater using deep eutectic solvent based extraction and flame atomic absorption spectrometry. *Analytical Letters, 1–11*. https://doi.org/10.1080/00032719.2020.1789871

Tobiasz, A., & Walas, S. (2014). Solid-phase-extraction procedures for atomic spectrometry determination of copper. In *TrAC -. Trends in Analytical Chemistry* (Vol. 62,, 106–122. https://doi.org/10.1016/j.trac.2014.06.018

Trindade, J. S., Lemos, V. A., Mata Cerqueira, U. M. F., Novaes, C. G., Araujo, S. A., & Bezerra, M. A. (2021). Multivariate optimization of a dispersive liquid-liquid microextraction method for determination of copper and manganese in coconut water by FAAS. *Food Chemistry, 365*. https://doi.org/10.1016/j.foodchem.2021.130473

Wang, N., Dai, H., Wang, D., Ma, H., & Lin, M. (2017). Determination of copper ions using a phytic acid/polypyrrole nanowires modified glassy carbon electrode. *Materials Science and Engineering C, 76*, 139–143. https://doi.org/10.1016/j.msec.2017.03.077