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Determination of Trace Levels of Cu^{2+} Using Ultrasonicated Dispersive Liquid Phase Microextraction Based on Deep Eutectic Solvents Followed by Flame Atomic Absorption Spectrometry

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Abstract

In this paper, liquid phase microextraction technique based on deep eutectic solvent was used for preconcentration of trace levels of Cu^{2+} followed by its determination by flame atomic absorption spectrometry (FAAS). 8-Hydroxy quinolone (oxine) was used as a complexing agent and the mixture of choline chloride-phenol with a mole ratio of 1:3 was used as an extraction solvent. By using ultrasonicated dispersive liquid phase microextraction technique, the extraction solvent was dispersed in the sample solution and extracted the hydrophobic complex in a short time. Different parameters affecting the relative recovery including pH of sample solution, concentration of complexing agent, mole ratio of extraction solvent component, volume of extraction solvent, extraction time and volume of aprotic solvent (tetrahydrofuran) were completely investigated and optimized. Under the optimum conditions, the calibration curve was linear in the range of 20-300 µg L^{-1} Cu^{2+} with a limit of detection of 4.5 µg L^{-1} Cu^{2+} (n=8). Also, the relative standard deviation based on seven replicate analysis of solution containing 50 µg L^{-1} Cu^{2+} was 3.1%. Finally, the proposed efficient, rapid and green liquid phase microextraction was successfully used for determination of trace levels of Cu^{2+} in different water samples.

Keywords
Copper (Cu^{2+}); Ultrasonicated based dispersive liquid phase microextraction; Deep eutectic solvent; 8-hydroxy quinolone (oxine)

1.INTRODUCTION

Copper (Cu) is one of the first metals ever extracted and used by humans; it has made vital contributions to sustaining and improving society since the dawn of civilization. Cu has widespread application in different industries such as pharmaceuticals [1], manufacturing of batteries [2], electronic equipment, alloys and cables [3]. Also, it is an essential trace element in both humans and animals. Cu is a co-factor of many redox enzymes [4] and has myriad of biological processes such as antioxidant defense, neuropeptide synthesis and immune function [5]. Dietary Cu deficiency can result in adverse consequences throughout the life span. Also, Cu deficiency may result in impaired development of the cardiovascular system, bone malformation, ongoing neurologic and immunologic abnormalities into infancy and beyond [6]. Therefore, determination of accurate levels of Cu in different real samples is an important demand. Liquid phase microextraction (LPME) is one of the most applicable sample preparation techniques which has several advantages such as rapidity, simplicity, low cost, high enrichment factor and high efficiency [7-9]. Ultrasonicated dispersive liquid phase microextarction (UDLPME) is a kind of LPME technique which used ultrasnoication waves for dispersion of extraction solvent into the sample solution at a short time. Up to now, different extraction solvents were used in LPME techniques, however, most of them such as chlorinated solvents are very harmful for living organism and environment. Therefore, application of green and environmentally friendly extraction solvents is highly demanded [10].

A new category of ionic solvents known as deep eutectic solvents (DESs) have been introduced by Abbot et al. (2003) [11, 12]. DESs are usually obtained from the mixture of a hydrogen bond acceptor (HBA) such as the non-toxic quaternary ammonium salt (e.g. Choline chloride) and a naturally-derived uncharged hydrogen bond donor (HBD), e.g. amines, sugars, alcohols, and carboxylic acids in a specific molar ratio [13-16]. DESs are non-toxic, environmentally friendly and have a negligible vapor pressure [17]. Choline chloride (ChCl) is a type of water-soluble vitamin

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B that is widely used as an animal feed supplement and can be either obtained from biomass or readily synthesized from fossil reserves via a simple process [18-21].

In this paper, 8-Hydroxy quinolone (oxine) was used as a complexing agent and the mixture of choline chloride-phenol with a mole ratio of 1:3 was used as an extraction solvent. By using UDLPME technique, the extraction solvent was dispersed in the sample solution and extracted the hydrophobic complex in a short time. Different parameters affecting the relative recovery (RR) including pH of sample solution, concentration of complexing agent, mole ratio of extraction solvent component, volume of extraction solvent, extraction time and volume of aprotic solvent (tetrahydrofuran) were completely investigated and optimized. The proposed rapid, highly rapid and efficient liquid phase microextraction was used for determination of trace levels of Cu2+ in different water samples.

2.EXPERIMENTAL

2.1. Instrument

A Shimadzu AA-670 (Shimadzu, Japan) flame atomic absorption spectrometer equipped with a 100 mm burner head, deuterium background correction and an air acetylene flame was utilized. A copper hollow cathode lamp (Shimadzu, Japan) operated at a current of 12 mA and a wavelength of 324.8 nm with a spectral bandwidth of 0.7 nm was used. The pH values in the aqueous phase were measured with Metrohm 827 pH lab (Switzerland) glass-electrode pH meter. Phase separation was assisted using Centurion Scientific Centrifuge (model Andreas Hettich D72, Tuttlingen, Germany) and a SONICA 2200 ETH (Italy) ultrasonic bath was used for dispersion of extraction solvent into the aqueous solution.

2.2. Reagents and Solutions

8-Hydroxy quinolone (oxine), choline chloride (ChCl, 99.5%), phenol (Ph, 99.5%), HNO_3 (65.0%) and NaOH (> 97.0%) and all nitrate salts were prepared from Merck (Darmstadt, Germany). Tetrahydrofuran (99.5%) as an aprotic solvent was purchased from Merck, Germany.

Deionized water was used throughout the analysis and all experiments was performed at 27 ± 2°C. Stock solutions of Cu^{2+} ions (1000 mg L^{-1}) were prepared by dissolving appropriate amounts of copper nitrate hexa-hydrate in 1 % (v/v) HNO_3.

2.3. Sample preparation

2.3.1. Water samples

Tap (Mashhad and Neyshabur. Iran), river (Kashaf Rood, Mashhad, Iran), spring (Nowchah, Mashhad, Iran) and mineral water samples were collected, filtered immediately through a Whatman filter paper (of 0.45-μm pore-size), and kept at 4 °C before analysis. The sample solutions were then analyzed for their Cu^{2+} content according to the microextraction procedure.

2.3.2. Deep eutectic solvent preparation

ChCl as HBA and Phenol as HBD were used for the synthesis of DES (with a 1:3 mole ratio of HBA:HBD). For each DES, the mixture was stirred at room temperature until a homogeneous liquid was obtained [22]. The prepared deep eutectic solvents were used in the proposed for UALPME technique.

2.3.3. Ultrasonicated dispersive liquid phase microextraction (UDLPME) technique

10 mL of a sample solution containing 100 μg L^{-1} Cu^{2+} and 10×10-4 mol L^{-1} oxine as a complexing agent was adjusted at pH 6.0. Then 500 μL of a mixture of choline chloride and phenol (ChCl:Ph), as the extraction solvent, was injected into a glass test tube and mixed for 1 min. An aliquot of 500 μL of THF was added to the solution which causes to the formation of cloudy solution and ultrasonicated for 4 min to completely disperse the extraction solvent into the sample solution. In order to accelerate the phase separation, the solution was centrifuged for 5 min at 3500 rpm. After this step, the aqueous phase was discarded using a syringe, and the extraction solvent (320 μL extraction solvent) was diluted to 400 μL with ethanol and aspirated into the FAAS for determination of the Cu.

3.RESULTS AND DISCUSSION

3.1. Optimization of extraction solvent

As explained before, ChCl as HBA and phenol as HBD were used for the synthesis of DES. The mole ratio of HBA(ChCl):HBD(Ph) has a significant effect on the extraction efficiency of DES. Therefore, different mole ratios of 1:1, 1:2, 1:3, 1:4 and 1:5 HBA:HBD were tested and the results are presented in Fig. 1. Based on the results, the mole ratio of 1:3 HBA:HBD provided a maximum extraction efficiency for Cu^{2+}. Therefore, for further experiments, HBA:HBD with a 1:3 mole ratio was selected as the optimum value.

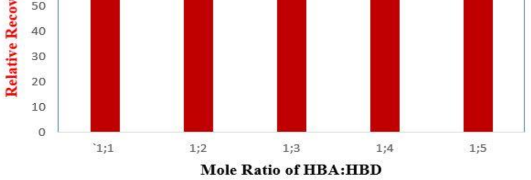

Fig. 1. Effect of mole ratio of HBA:HBD on the RR of Cu^{2+}.

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3.2. Effect of pH

pH of sample solution is one of the main parameters affecting the stability of the metal-complexing agent complex; therefore it has an important effect on the RR of analyte. The effect of pH on the RR of Cu^{2+}-oxine complex was investigated in the range of 2-9. The obtained results show that (Fig 2), by increasing the pH of sample solution up to 6, the RR increases which may be related to the instability of Cu^{2+}-oxine complex in acidic media. However, higher pH values than 6 cause to the decrease in RR of Cu^{2+} which may be due to the formation of $Cu(OH)^2$ in the sample solution. Therefore, for further studies, pH=6 was selected as the optimum value.

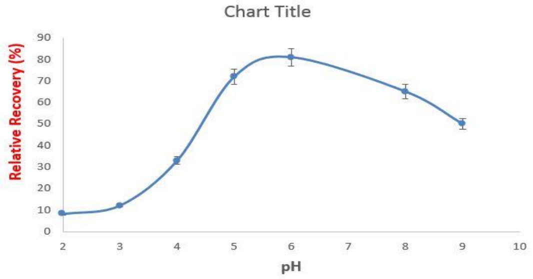

Fig. 2. Effect of pH of sample solution on the RR of Cu2+. Conditions: Cu^{2+}: 100 µg L^{-1}, 10×10^{-4} mol L^{-1} Oxine, 500 µL extraction solvent, 500 µL THF, 4 min extraction time

3.3. Effect of the concentration of complexing agent

In this research, 8-hydroxy quinolone (oxine) was used as a complexing agent to from a hydrophobic complex with Cu^{2+}. Therefore, its sufficient concentration in the sample solution is a key factor to obtain high RR. The concentration of oxine was studied in the range of $1\times10^{-4-2}\times10^{-3}$ mol L^{-1} and the obtained results are presented in Fig 3. According to the obtained results, the RR increases by increasing of the concentration of Oxine up to 7.5×10^{-4} mol L^{-1} and it remains constant afterwards. Therefore, for further experiments the concentration of 10×10^{-4} mol L^{-1} Oxine was considered as the optimum value.

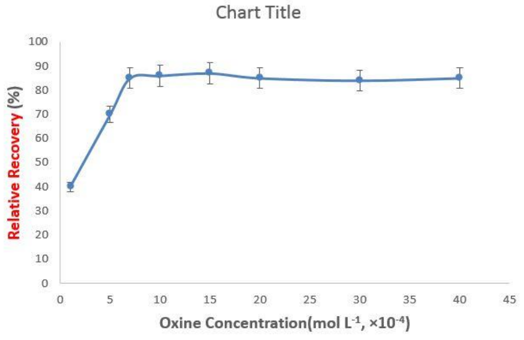

Fig. 3. Effect of the concentration of oxine on the RR of Cu^{2+}. Conditions: Cu^{2+}: 100 µg L^{-1}, pH 6, 500 µL extraction solvent, 500 µL THF, 4 min extraction time

3.4. Effect of the volume of extraction solvent

In order to optimize the volume of extraction solvent (ChCl:Ph), different volumes of extraction solvent in the range of 300-700 µL were tested. The obtained results in Fig 4 show that by increasing the volume of extraction solvent the RR increases which could be related to the increasing of the surface area of the extraction solvent to extract the hydrophobic complex of Cu^{2+}-oxine. Therefore, according to the results, 500 µL of the extraction solvent was considered as the optimum value.

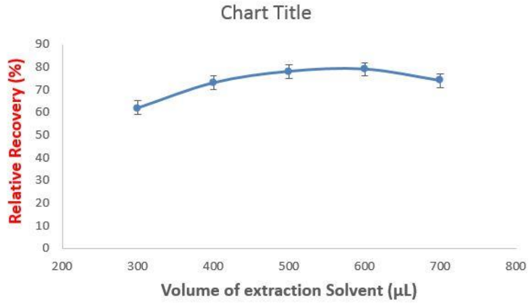

Fig. 4. Effect of the extraction solvent volume on the RR of Cu^{2+}. Conditions: Cu^{2+}: 100 µg L^{-1}, 10×10^{-4} mol L^{-1} Oxine, 500 µL THF, 4 min extraction time.

3.5. Extraction time

Extraction time is another important parameter affecting the RR of analyte in LPME techniques. Since the ultrasonication technique was used for dispersion of extraction solvent in the sample solution, therefore, by formation of fine droplets of the extraction solvent, the surface to area increases dramatically and the extraction of analyte takes place in a short time. The effect of extraction time was studied by investigation of different ultrasonication time in the range of 1-10 min. According to the results in Fig 5, maximum RR was obtained after 4 min ultrasonicate time which clearly shows that the proposed method is highly rapid technique for extraction of analyte. Therefore, for further experiments, 4 min extraction time was considered as the optimum value.

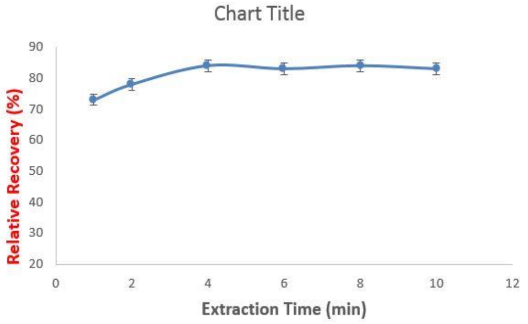

Fig. 5. Effect of extraction time on the RR of Cu^{2+}. Conditions: Cu^{2+}: 100 µg L^{-1}, 10×10^{-4} mol L^{-1} oxine, 500 µL extraction solvent, 500 µL THF.

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3.6. Effect of the volume of THF

THF as an aprotic solvent was used to reduce the solubility of the extraction solvent in the sample solution. The effect of the volume of THF on the RR of Cu^{2+} was studied in the range of 300-700 µL and the obtained results are presented in Fig 6. According to the results, low RR for Cu^{2+} obtained at low volumes of THF, however by increasing of the volume of THF to 500-600 µL, the RR increases and reaches to its maximum value. Therefore, for further experiment, 500 µL THF was selected as the optimum value.

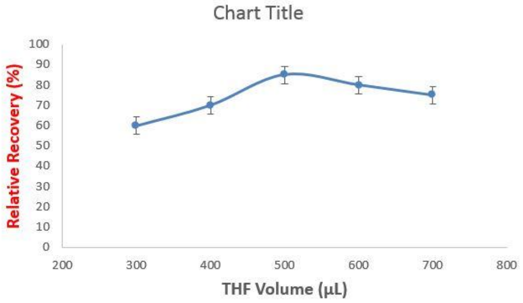

Fig. 6. Effect of the volume of THF on the RR of Cu^{2+}. Conditions: Cu^{2+}: 100 µg L^{-1}, 10×10^{-4} mol L^{-1} oxine, 500 µL extraction solvent, 4 min extraction time.

3.7. Effect of ionic strength

In order to investigate the effect of ionic strength on the RR of Cu^{2+}, different concentrations of NaCl and $NaNO_3$ in the range of 0-1% (g mL^{-1}) were studied and the results are presented in Fig 7. According to the results, no serious changes in the RR of Cu^{2+} was observed up to 0.4% g mL^{-1} NaCl and 0.2 % g mL^{-1} $NaNO_3$. However, higher concentration of salt ions cause to the decrease of the RR of Cu^{2+} which could be related to the increasing of the viscosity of the sample solution and insufficient dispersion of extraction solvent into the sample solution [20].

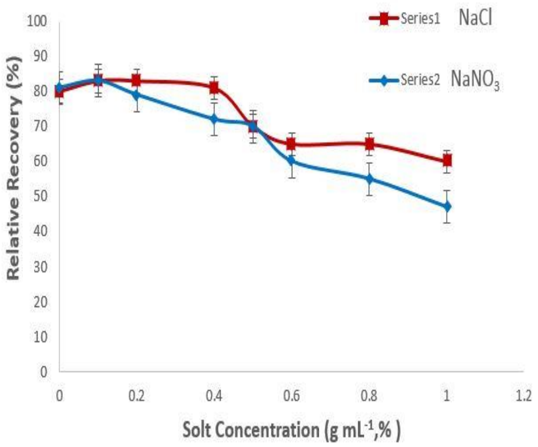

Fig. 7. Effect of ionic strength of sample solution on the RR of $Cu2^{+}$.

3.8. Effect of interfering ions

The effect of different ions on the RR of Cu^{2+} was studied in details and the obtained results are presented in Table 1. Ion was consider as interfere if it causes to decrease of the RR of Cu^{2}+ more than ± 5%. The obtained results show that, no serious interfere was exist for preconcentration of Cu^{2+} which clearly show that the proposed method has acceptable selectivity for determination of Cu^{2+} in different water samples.

Table 1. Effect of interfering ions on the relative recovery of 100µg L^{-1} Cu^{2+}. (Recovery: mean ± standard deviation based on three replicate analysis)

Interfering ions	Added as	Concentration (µg L^{-1})	Relative Recovery (%)
Mg^{2+}	$Mg(NO_3)_2.9H_2O$	50000	96.1
Al^{3+}	$Al(NO_3)_3.9H_2O$	500	97.6
Zn^{2+}	$Zn(NO_3)_2$	500	95.1
Co^{2+}	$Co(NO_3)_2.6H_2O$	500	98.8
Fe^{3+}	$Fe(SO_4)_2.NH_4.12H_2O$	500	95.0
Mn^{2+}	$MnSO_4.H_2O$	500	97.1
Ni^{2+}	$Ni(NO_3)_2$	500	98.8
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	500	99.0
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	400	96.6
Pb^{2+}	$Pb(NO_3)_2$	500	99.3
SO^{42-}	K_2SO_4	75000	95.3

3.9. Analytical Figures of Merit

Under the optimum condition, the calibration curve after preconcentration was linear in the range of 20 - 300 µg L^{-1} Cu^{2+} with a correlation coefficient of 0.9893. The equation of calibration curve after preconcentration step is A= 0.0016CCu2+-0.0154 where A is the absorbance of Cu and CCu^{2+} is the concentration of Cu^{2+} ion in µg L-1. The relative standard deviation based on seven replicate analysis of 50 µg L^{-1} Cu (II) was 3.1 % and the detection limit (n=8) was 4.5 µg $^{L-}$1. The preconcentration factor (PF) was calculated based on the volume of sample solution (10 mL) to the final solution aspirated into the FAAS (0.4 mL) which equal to 25. The enhancement factor (EF) was 22.5, defined as the slope of the calibration curve after preconcentration step to that of before preconcentration step (A= 0.0667 CCu 2++0.0029).

3.10. Analysis of real samples

The proposed method was used for preconcentration of trace levels of Cu2+ in different water samples. The obtained results are presented in Table 2. Also, spike test was also performed on the samples to check the validity of the obtained results. As it could be seen, acceptable recoveries in the range of 96.2-102.2 % were obtained for determination of Cu^{2+}.

Table 2. Determination of Cu^{2+} ions in different water samples (mean ± standard deviation based on three replicate analyses).

Sample	Added (ng mL^{-1})	Found (ng mL^{-1})	Relative Recovery (%)
Tap water, Mashhad, Iran	-	ND	-
	50.0	49.4 ± 2.5	98.8
Spring water, Nowchah, Mashhad, Iran	-	ND	-
	50.0	51.1 ± 1.3	102.2
Tap water, Neyshabur, Iran	-	ND	-
	50.0	48.1 ± 1.6	96.2
Kashaf Rood, Mashhad, Iran	-	33.2 ± 1.3	-
	50.0	81.7 ± 3.2	97.0
Mineral water	-	ND	-
	50.0	50.5 ± 2.1	101.0

ND: Not detectable

Table 3. Comparison of the proposed method with other procedures

Method	Sample	LOD (μg L^{-1})	Linear range (μg L^{-1})	RSD%	Recovery%	Ref.
DLLME	Real water, Food	1.23	-	0.9	96-104	[8]
DSPME	Real water	20	-	≤3.3	89-95	[23]
MSPE	Real water	24.5	300-2200	-	95	[24]
IL-SDME	Real water	0.15	5-50	3.4	98-105	[25]
DLLME	Real water	0.48	0.2-100	4.9	95.6-101.3%.	[26]
DLLME	Real water	0.3	1-200	≤5.7	97-105	[27]
UDLPME	Real water	4.5	20 - 300	3.1	98-102.2	This work

DSPME : Dispersive solid phase microextraction; MSPE: Magnetic solid phase extraction; IL-SDME: Ion liquid -single drop microextraction; UDLPME: Ultrasonicated dispersive liquid phase microextraction

3.11. Comparison of the method with previous procedures

The proposed method was compared with other microextraction methods [8, 23-27] in term of linearity, LOD, RSD and recovery for the determination Cu^{2+} ion (Table 3). The proposed method showed a wide linear range, low detection limit. One of the important advantages of the method compared to other selected methods was the significant reduction in analysis time. Other benefits of the method include simple operation and low cost.

4.CONCLUSION

The proposed paper describes the application of ultasonicated based dispersive liquid phase microextraction for preconcentration (UDLPME) of trace levels of Cu^{2+} followed by its determination using FAAS. 8-Hydroxy quinolone (oxine) was used as a complexing agent to form a hydrophobic complex with Cu^{2+} and a mixture of choline chloride-phenol as a DES was used as extraction solvent. To extract the hydrophobic complex of Cu^{2+}-oxine, UDLPME technique was used. The main parameters affecting the RR of Cu^{2+} including pH of sample solution, concentration of oxine, extraction time, volume of extraction solvent and the volume of THF were investigated and under the optimum conditions, the calibration curve was obtained in the range of 20 - 300 µg L-1 Cu^{2+}. The main advantages of the proposed method are high efficiency, wide dynamic range, short analysis time, green approach and low cost.

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Compliance with ethical standards

Conflict of Interest

The authors confirm that there are no known conflicts of interest related to this publication and this work has not received any significant financial support to influence its outcome.

Ethical Approval

This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent

Informed consent is not applicable to this study.

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food and water samples before spectrophotometric determination, *Spect. Acta Part A.* 79 (2011) 1941.

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اندازه گیری مقادیر کم Cu^{2+} با استفاده از میکرواستخراج فاز مایع پراکنده فراصوت بر اساس حلالهای یوتکتیک عمیق همراه با طیف سنجی جذب اتمی شعله

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چکیده

در این مقاله، تکنیک میکرواستخراج فاز مایع مبتنی بر حلال یوتکتیک عمیق برای پیش تغلیظ مقادیر کم Cu^{2+} و سپس تعیین آن توسط طیف‌سنجی جذب اتمی شعله (FAAS) استفاده شد. ۸-هیدروکسی کینولون (اکسین) به عنوان یک عامل کمپلکس کننده و مخلوط کولین کلرید-فنل با نسبت مولی ۱:۳ به عنوان حلال استخراج کننده استفاده شد. با استفاده از تکنیک میکرو استخراج فاز مایع پراکنده اولتراسونیک، حلال استخراج کننده در محلول نمونه پراکنده شد و کمپلکس آبگریز در مدت زمان کوتاهی استخراج شد. پارامترهای مختلف موثر بر بازیافت استخراج شامل pH محلول نمونه، غلظت عامل کمپلکس کننده، نسبت مول اجزای حلال استخراج کننده، حجم حلال استخراج کننده، زمان استخراج و حجم حلال آپروتیک (تتراهیدروفوران) به طور کامل بررسی و بهینه شدند. در شرایط بهینه، منحنی کالیبراسیون خطی در محدوده ۲۰-۳۰۰ میکروگرم بر لیتر Cu^{2+} با حد تشخیص 4.5(n=8) میکروگرم برلیتر بود. همچنین انحراف معیار نسبی بر اساس آنالیز هفت تکرار محلول حاوی ۵۰ میکروگرم در لیتر Cu^{2+} 3.1 درصد بود. در نهایت، میکرواستخراج فاز مایع سبز کارآمد، سریع با موفقیت برای تعیین مقادیر کم Cu^{2+}در نمونه‌های مختلف آب مورد استفاده قرار گرفت.

کلید واژه ها

مس (Cu^{+2})؛ میکرواستخراج فاز مایع پراکنده مبتنی بر اولتراسونیک؛ حلال یوتکتیک عمیق؛ ۸-هیدروکسی کینولون (اکسین)

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