Determination of Copper Using Supramolecular Solvent-based Microextraction for Food, Spices, and Water Samples Prior to Analysis by Flame Atomic Absorption Spectrometry

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INTRODUCTION

Copper (Cu) is one of the most important essential trace elements. Foods such as olives, almonds, beans, grapes, and wheat contain copper. Copper plays an important role in the metabolism and is very active for some biological processes, especially in the synthesis of red blood cells (1-4). The metal is also necessary for enzymes whose duties are renewing body tissues and contribute to the strength of the bone structure. It takes charge in protein synthesis and energy production. Deficiency of copper results in anemia, decreased body resistance to illnesses, weakness, even forming scars on skin and causing eczema. Despite the fact that copper is an essential trace element when it is taken at high levels, it can also produce toxic effects. For instance, causing harm to organs such as the brain and pancreas, and mental and physical sickness such as depression, high blood pressure, and cancer (5, 6).

Copper also has industrial uses due to its high electrical and thermal conductivities, good durability and ductility, with perfect resistance to corrosion. Hence, can become a very real concern for environmental pollution in wastewater and the environment in general. Thus, monitoring of trace

ABSTRACT

A simple and sensitive supramolecular solvent microextraction method was developed for the separation, preconcentration and determination of trace levels of copper in food and environmental samples. The supramolecular solvent system consists of tetrahydrofuran (THF) and undecanol and was used as an extraction solvent for the microextraction procedure of Cu(II). A supramolecular solvent microextraction procedure for copper(II) as its 5-methyl-4-(2-thiazolylazo) resorcinol (5-ME-TAR) complex was established prior to micro-sampling flame atomic absorption spectrometric determination. The influence of various analytical parameters including pH, solvent type and volume, amount of 5-methyl-4-(2-thiazolylazo) resorcinol, and centrifugation time were investigated. The effects of certain alkali, alkaline earth, and transition metal ions on the quantitative extraction of copper(II) were also studied.

The proposed supramolecular solvent-based microextraction procedure exhibits a limit of detection (LOD) of $1.4 \mu\text{g L}^{-1}$ and a limit of quantification (LOQ) of $4.6 \mu\text{g L}^{-1}$. A preconcentration factor of 60 was obtained and the relative standard deviation was 2.78%. The method was validated by the analysis of certified reference materials and applied to food, spices, and water samples.

levels of copper in samples from industrial wastewater, biological and food samples (7) is very important. Copper is also obtained from sulfur ore requiring negative enrichment, an expensive process and of concern for environmental pollution.

Because of the low levels of copper in food, water, and ores as well as interference from matrix components, reliable and sensitive analytical methods are required for its determination (8). For this purpose, analytical methods such as atomic absorption spectrometry (FAAS), X-ray fluorescence (XRF), neutron activation analysis (NAA), inductively coupled plasma atomic emission spectrometry (ICP-AES), electrothermal atomic absorption spectrometry (ETAAS), voltammetry and inductively coupled plasma-mass spectrometry (ICP-MS) have been commonly used (9).

However, for trace metals analysis with any of the above methods, an enrichment procedure has to be applied. In this study, flame atomic absorption spectrometry (FAAS) has been selected which also requires a sample preparation method. Since the concentration of copper is generally very low in environmental, food, ore samples and due to matrix effects, a number of effective separation and enrichment methods have been developed (10). For instance, adsorption, cloud point extraction (CPE), liquid-liquid extraction (LLE).

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These methods have the disadvantage of requiring considerable amounts of chemical solvents, have small preconcentration factor, and are time-consuming. Hence, microextraction methods such as dispersive liquid-liquid microextraction (DLLME), supramolecular solvent-based microextraction (SS-LLME), and single drop microextraction (SDME) have become popular. In this study, the supramolecular solvent-based microextraction process was used for the separation/preconcentration of trace levels of copper.

The supramolecular liquid phase microextraction is based on the self-assembly process of two or more solvents having a long carbon chain containing hydroxyl and carboxylic acid groups in their structure. Supramolecular solvent liquid-liquid microextraction (SS-LLME) occurs at a molecular and nano-sized level from a homogenized solution containing amphiphilic groups (11-13). Supramolecular solvents create a perfect reaction setting for the extraction process. Thus, these solvents composed of nano-sized micelles interact more with the analyte. They provide high extraction efficiency. The method is generally applied to the extraction of metals and hydrophobic organic compounds in environmental and biological aqueous samples (11-13). It is environmentally friendly, with a short extraction time, no harmful waste generation, easily applicable, accessible, and a fast low-cost liquid phase extraction technique (14).

With this microextraction method, the high efficient ligands are sorbents to remove the copper ions from the aqueous solution. 5-ME-TAR is one of the ligands containing a resorcinol scaffold. Its respective formula and molecular weight are $C_{10}H_9N_3O_2S$, 235.26 g/mol. The 5-ME-TAR can be applied for the determination of various transition metal ions, such as Cu^{2+} , Pd^{2+} , Ni^{2+} , Zn^{2+} , Hg^{2+} , etc.

The complexes of 5-ME-TAR with these metals have a higher molar absorptivity (15, 16). The 5-ME-TAR resorcinol ligand with many nitrogen and oxygen donor atoms binds the metal cations (17).

In this work, a new, simple, and rapid supramolecular system procedure has been established for the separation and preconcentration of Cu(II) with 5-methyl-4-(2-thiazolylazo) resorcinol (5-MeTAR) complex before determination by microsampling flame atomic absorption spectrometry. The analytical parameters for quantitative extraction were optimized, and recoveries up to 95% were achieved. In addition, the method was validated by the analysis of certified reference materials and applied to food and water samples.

EXPERIMENTAL

Instrumentation

A PerkinElmer AAnalyst™ 300 flame atomic absorption spectrometer from (PerkinElmer, Inc., Shelton, CT, USA) was used for this study. The instrument was equipped with an air-acetylene flame with a 10 cm long slot burner head. Hollow cathode lamps were used for copper. A PHS-3C pH meter (pH-900, Ankara, Turkey) with a combined glass electrode was utilized to determine the pH values. The distilled water was obtained with a Millipore Milli-Q® system (18MΩ-cm resistivity, Millipore Corporation, Bedford, MA,

USA). Also, a model ALC PK 120 centrifuge (Buckinghamshire, England) and a Vortex mixer (Wiggen Hauser, Selangor, Malaysia) were used. The instrumental parameters for flame atomic absorption spectrometry analysis are listed in Table I.

Reagents and Standard Solutions

The diluted standard solutions were prepared from a stock standard copper solution of 1.00 mg L⁻¹ $Cu(NO_3)_2$ in HNO_3 was obtained from Merck, Darmstadt, Germany. Working solutions were prepared daily from the stock solutions by serial dilution with distilled water (18). A solution of 5-methyl-4-(2-thiazolylazo) resorcinol (5-ME-TAR) was prepared in ethanol (Aldrich 95%). In addition (5-ME-TAR) solution of 0.025% was prepared by dissolving 0.025 g of (5-ME-TAR) in 100 mL of ethanol. Within the pH range of 4 to 8, the pH values were adjusted by addition of HAc-NaAc, borate and ammonia buffer solutions. Accuracy of the method was studied by examining the standard analytical reference materials TMDA 53.3 (Canada Lake Water) and NCSZC73032 Celery (P.R. China). Also, 0 – 8 µg/L standard solutions were used. All chemicals and analytical grade solutions were prepared in deionized water.

Procedure

An amount of 4 µg Cu(II) was taken into a 50-mL centrifuge tube, then 2 mL of acetate buffer solution was added to adjust the sample pH to 6. After pH regulation, 400 µL THF and 200 µL undecanol were added quickly to the Cu(II) sample solution to form the supramolecular solvent. After these steps, the sample solution of Cu(II) was sonicated for 3 minutes, and a cloudy solution was obtained. After continuing the ultrasonication process, the supracellar solvent solution passing through the molecular

TABLE I
Instrumental Operating Conditions Used for FAAS Analysis

Element	Cu
Wavelength	324.8 nm
Slit width	0.7 nm
Lamp current	15 mA
Flame conditions:	
Air	9.5 L/min
Acetylene	2.3 L/min

casing was blurred. The cloudy solution was centrifuged at 4000 rpm for 10 minutes. Then, the solvent phases were completely separated from the aqueous phase and formed a solvent solution in the upper phase. The lower water phase was eliminated with an injector. After the liquid phase was removed from the solution, the remaining phase volume was between 200 and 300 μL . The supramolecular solvent (about 200–300 μL) was completed to 500 μL with ethanol. The final solution was optimized using the developed microextraction method and analyzed by flame atomic absorption spectrometry.

RESULTS AND DISCUSSION

Effect of pH

Since extraction of the material from the water phase to the extraction phase depends on the pH value of the medium at the trace level, the model solutions were prepared at different pH values (4–8) with the help of a buffer solution in order to determine the optimum pH range for the quantitative extraction of copper. Therefore, all subsequent studies were performed at pH 6. Later, the microextraction method was applied to the specimens using the

atomic absorption spectrometer. Quantitative recoveries ($R \geq 95\%$) were obtained for copper at pH 6. The optimum sample solution pH was chosen at 6, and the subsequent work was continued at pH 6 (Figure 1).

Effect of Volume Ratio of Undecanol and THF

The supramolecular solvent is obtained by mixing species that have a long carbon chain, including carboxylic acid ($-\text{COOH}$) and the hydroxyl ($-\text{OH}$) group with organic solvents such as THF or tetrabutylammonium. Initially, we decided which supramolecular solvents to use for the preconcentration of copper. For this reason, preconcentration of copper, the effects of non-molecular, water-immiscible and micelle-forming organic solvents were generated. After this parameter, the amount of supramolecular solvents, which have been chosen to obtain the best recovery value, were investigated. The supramolecular solvent-based microextraction method with undecanol was selected since the recovery values of 95% or more were obtained.

One of the most important parameters is the volume of extraction solvent that seriously affects the

efficiency of extraction performance (19). A volume of 50–400 μL undecanol was prepared before determining the optimal volume to be present in the supramolecular solvent. The results are given in Figure 2. As can be seen, the quantitative undecanol volume was 200 μL .

In addition, the influence of THF volume, required to be present in the supramolecular solvent, was studied for the recovery of copper. For this, the supramolecular solubilizers were prepared in which the volume of undecanol was fixed to 200 μL and the volume of THF was changed. A THF volume between 200–600 μL was chosen, and the final optimum THF volume selected was 400 μL . The volume of tetrahydrofuran was kept constant at 0.4 mL (Figure 3).

As a result, further experiments were carried out using 200 μL of undecanol and 400 μL of THF, followed by separation-enrichment by microextraction with the supramolecular solvent.

Effect of Amount of Ligand

For this parameter, the optimum amount of 5-methyl-4-(2-thiazolylazo) resorcinol (5-ME-TAR) ligand was investigated. For this, the extraction was carried out by

Fig. 1. Effects of pH on the recoveries of copper ($N=3$).

Fig. 2. Effects of undecanol volume on the recoveries of copper ($N=3$).

adding the amount of ligand from 0 to 0.25 mg in sample solutions. It was found that the preconcentration of copper was quantitative using above 0.2 mg of the ligand and the recovery values were 96–97%. Thus, 0.2 mg of the ligand was chosen for all subsequent extractions. The experimental results are shown that Figure 4.

Effect of Sample Volume and Centrifugation Time

The supramolecular solvent-based microextraction method was carried out in the range of 10–40 mL of sample volume at the optimized conditions of pH 6, amount of ligand 0.2 mg (0.025%), and final volume of 0.5 mL in order to calculate the preconcentration factor, as shown in Figure 5. Although the recovery values for the 30 mL sample volume were quantitative, the recovery values were beginning to decrease when the sample was prepared with a higher volume value. Thus, the preconcentration factor was calculated as 60, considering the last volume was 500 μ L.

The effect of centrifugation time was also investigated in the range of 5–15 minutes. Quantitative recovery of Cu(II) was achieved in 10 minutes. A centrifugation speed and time of 4000 rpm and 10 minutes, respectively, were selected for further experiments for Cu(II).

Matrix Effects

The effects of alkaline, earth alkaline, and some anions cause matrix effects in the flame atomic absorption spectrometric determinations of trace level copper. Therefore, researching the matrix effects of foreign ions are one of the most important parameters. In addition, this parameter verifies the selectivity of the method for the preconcentration and separation of the Cu(II) ions. The tolerance concentrations of each of the foreign ions mentioned before were investigated and the recovery values

were calculated. The obtained results are summarized in Table II.

Analytical Performance

The analytical parameters of the supramolecular solvent-based

microextraction method for Cu(II) using the optimum conditions are shown in Table III. Also, the analytical performance criteria such as limit of quantification (LOQ), limit of detection (LOD), relative stan-

Fig. 3. Effects of THF volume on the recoveries of copper ($N = 3$).

Fig. 4. Effects of 5-methyl-4-(2-thiazolylazo) resorcinol (5-MeTAR) amount on the recoveries of copper. ($N = 3$).

Fig. 5. Effects of sample volume on the recoveries of copper ($N = 3$).

dard deviation (RSD), correlation co-efficient (R^2), and the preconcentration factor (PF) for copper were examined under the optimized experimental conditions. Furthermore, quantitative recovery values fall below 10 mL, and above 30 mL was not obtained. The developed supramolecular solvent-based microextraction procedure exhibits a limit of detection (LOD) of $1.4 \mu\text{g L}^{-1}$ (LOD by using the 3 s/m formula) and a limit of quantification (LOQ) of $4.6 \mu\text{g L}^{-1}$ (LOQ was calculated by using the 10 s/m formula). The preconcentration factor was found at 60 (20). The linear

calibration curve was obtained using equation $A = 0.1947C - 0.004$, $r^2 = 0.9993$ [A = mean absorbance and C = the concentration of Cu(II) $\mu\text{g L}^{-1}$].

Precision is important for the preconcentration of copper. Because of this, the relative standard deviation (RSD), determined from standard solution of copper was 2.78 % ($\text{RSD} = s/x$).

Analysis of Certified Samples

The accuracy of the proposed method was verified using the analysis of two certified reference

materials (CRMs): TMDA 53.3 Food (China National Analysis Center, P.R. China) and NCSZC73032 Celery (National Water Research Institute, Canada). Initially, 2 mL of TMDA 53.3 was prepared and added to the sample solution. Then, the developed preconcentration method was applied at optimum conditions (2 mL buffer solution, 0.2 mg 5-ME-TAR ligand, pH 6, and 1:2 undecanol-THF supra-molecular solvent). The CRM NCSZC 73032 Celery sample was analyzed, 75 mg placed into a beaker and 10 mL HNO_3 added, then evaporated to dryness. The mixture was allowed to cool, and then 5 mL of HNO_3 + 5 mL H_2O_2 were added and evaporated to dryness. The standardized reference material that was solubilized was extracted with 5 mL of distilled water. Then the supramolecular solvent was added, and the solution completed to 10 mL with distilled water. After these steps, the proposed supramolecular solvent-based microextraction method was applied. The calculated values are listed on Table IV. These values show that this method proves the accuracy of the microextraction method.

Analysis of Food and Water Samples

Different real samples, such as food and water, were analyzed by the developed microextraction procedure. The method proposed for addition/recovery has been applied to tap water, lake water, macaroni, opium poppy, thyme, and bread.

An amount of 1 g of each real sample (macaroni, opium poppy, thyme, and bread) was put into respective 50-mL beakers. Then, 10 mL HNO_3 was added for sample solubilization and evaporated to dryness with a manual heater. The dissolved and evaporated samples were left standing until cooled. At the end of this operation, 5 mL HNO_3 and 5 mL H_2O_2 were added to the samples, and evaporated in

TABLE II
Influences of Some Foreign Ions on the Recoveries of Cu

Foreign Ions	Added As	Concentration (mg L^{-1})	Recovery (%)
Na^+	NaNO_3	2500	103 ± 1^a
K^+	KCl	2500	98 ± 1
Mg^{2+}	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2000	100 ± 1
Ca^{2+}	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	2000	100 ± 0
Zn^{2+}	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	20	97 ± 1
Mn^{2+}	$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	20	95 ± 0.5
Cr^{3+}	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	20	98 ± 2
Cd^{2+}	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	20	102 ± 1
Cl^-	KCl	2500	98 ± 1
SO_4^{2-}	Na_2SO_4	2000	101 ± 1

^a Mean $\pm$ standard deviation.

TABLE III
Optimum Conditions for Supramolecular Solvent-based Microextraction of Cu

pH	6
Supramolecular solvent (THF:undecanol)	2:1 (400 μL :200 μL)
5-methyl-4-(2-thiazolylazo) resorcinol (5-MeTAR)	0.2 mg
Sample volume	30 mL
Final volume	500 μL
Centrifugation speed and time	4000 rpm, 10 min

Table IV
Application for Cu in CRMs

CRMs	Certified Value	Observed Value	Recovery (%)
TMDA 53.3	$312 \mu\text{g L}^{-1}$	$307 \pm 0.5 \mu\text{g L}^{-1}$	98
NCSZC73032 Celery	$8.2 \pm 0.4 \mu\text{g g}^{-1}$	$8.14 \pm 1.8 \mu\text{g g}^{-1}$	99

^a Mean $\pm$ standard deviation.

TABLE V

Application of Present Method to Food Samples

Samples	Added (µg/g)	Found (µg/g)	Recovery (%)
Macaroni	0.0	0.17± ^a 0.20	-
	1.0	1.16 ± 0.14	99
	2.0	2.15 ± 0.10	99
Opium poppy	0.0	0.16± 0.03	-
	1.0	1.17± 0.06	10199
	2.0	2.14± 0.03	99
Thyme	0.0	N.D. ^b	-
	1.0	0.99± 0.03	99
	1.5	1.44±0.05	95
Bread	0.0	0.12± 0.10	-
	1.0	1.11± 0.10	99
	2.0	2.17± 0.04	102

^a Mean ± standard deviations.^b N.D.: Not detected.

TABLE VII

Comparison of Present Method With Literature Values for Preconcentration of Cu

Preconcentration Method	Analysis Method	LOD ^a	PF ^b	Samples	Ref.
DLLME	AAS	0.19 µg L ⁻¹	135	Food, Water	21
SPE	UV-Vis	5 µg L ⁻¹	125	Water	22
DLLME	AAS	0.11 µg L ⁻¹	60	Water, Hair	23
DLLME	HPLC	7.9 µg L ⁻¹	50	Food, Vegetation, Water	24
DLLME	UV-Vis	0.81 µg mL ⁻¹	5	Water	25
Supramolecular solvent-based DLLME	AAS	1.4 µg L ⁻¹	60	Food, Spices, Water	This work

^a LOD: Limit of detection.^b PF: Preconcentration factor.

the same way until dry. These real samples were taken into tubes with distilled water after the solubilization operations were completed. Subsequently, the added/recovery operations were applied in order to implement the method. For this, three 50 mL sample tubes were prepared to apply the developed microextraction procedure. Then, 2.25 mL each of macaroni and

opium poppy and 1.5 mL of thyme and bread were added into each tube. Then, 0.0–2.0 µg/mL of copper was increasingly added, and the developed microextraction method applied. The optimized method was also applied to 30 mL of water sample. Finally, the analyte concentrations in the final volume were analyzed by flame atomic absorption spectrometry. The validation of

TABLE VI

Application of Present Method to Water Samples

Samples	Added (µg/g)	Found (µg/g)	Recovery (%)
Tap water	0.0	N.D. ^a	-
	1.0	1.02± ^b 0.06	102
	1.5	1.54± 0.02	103
Lake water	0.0	N.D.	-
	1.0	1.01± 0.03	101
	2.0	1.97± 0.08	98

^a N.D.: Not detected.^b Mean ± standard deviations.

the improved method was checked by the addition-recovery tests. The results listed in Table V for the food samples and in Table VI for the water samples show that good agreement was achieved between the added and recovered copper ions.

For this study, some previously reported methods were also investigated and compared with the proposed microextraction procedure (see Table VII). In comparison with other techniques for preconcentration of copper, the present study required a short extraction time and was performed at room temperature. Low limits of quantification (LOQ) and limits of detection (LOD) were found. A good preconcentration factor for copper was calculated at 60, resulting from a 0.5 mL sample volume up to 500 µL final volume. It was found that the method was optimized with simplicity, rapidity, high selectivity, and low cost and in a simple manner and little time.

CONCLUSION

This method has some advantages for the recovery of copper in food and water samples. For instance, good selectivity (there is no interaction effect in the presence of the matrix ions), the method is much simpler, faster, and low cost. Preconcentration/separation of the

trace level copper in real samples showed high level recovery values at above 95%. Furthermore, it is an environmentally sensitive method using very little organic solvent. The supramolecular solvent-based microextraction method is a rapid technique and time has no impact on the recovery of copper and extraction efficiency (26, 27). Also the ligand of 5-methyl-4-(2-thiazolylazo) resorcinol (5-ME-TAR) showed high affinity and good accessibility for Cu(II) ions. The matrix effects were remarkably tolerable for Cu(II). Due to these advantages, the method is practical and reliable for the preconcentration/separation of copper from environmental water and food samples.

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