

Supramolecular Solvent-based Microextraction of Copper at Trace Levels Before Determination by Microsampling Flame Atomic Absorption Spectrometry

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INTRODUCTION

Copper is present in nature from anthropogenic activities or from ore processing. Fine parts of copper may suspend in air as dust, which leads to the high probability of distribution in water surfaces and to contaminating the environment (1, 2). The presence of trace amounts of copper is essential for the human body. It plays an important role in the formation of hemoglobin as well as in the metabolism of carbohydrates (3). However, at high concentrations, copper becomes an adverse health effect and results in normocytic anemia and leukopenia. Exposure to high concentrations of copper over a long period of time may cause liver damage, anemia, and kidney disfunction (4-6).

The monitoring of copper in water samples has become a crucial need to ensure human safety (7, 8). Usually, copper can be detected by atomic absorption spectrometry (AAS), graphite furnace AAS (GFAAS), inductively coupled plasma mass spectrometry (ICP-MS). The difficulty associated with copper determination is due to matrix interference and the trace copper levels which leads to inaccurate results. However, preconcentration steps before instrumental detection may overcome these problems (9-17). Many sample pretreatment steps have been applied for copper preconcentration including solid phase extrac-

ABSTRACT

A microextraction method, based on the complexation of Cu(II) with N-Benzoyl-N,N-diisobutylthiourea, followed by phase separation by assistance of supramolecular solvents, was developed. The supramolecular solvent of tetrahydrofuran and 1-decanol enhanced the hydrogen bonding, in addition to the dispersion action leading to a quick phase separation with efficient preconcentration of copper(II) at trace levels. The developed procedure works at weak acidic medium (pH 3). The analytical parameters were optimized. The influence of concomitant ions on the recoveries of copper was also investigated. The proposed supramolecular-based procedure exhibits a limit of detection (LOD) of $0.46 \mu\text{g L}^{-1}$ as well as quantitative recoveries from water certified reference materials. The proposed procedure was applied to the determination of copper at trace levels in water samples obtained from various sources in Turkey.

tion (11), cloud point extraction (12), and dispersive liquid-liquid microextraction (9, 10).

Researchers are still focusing on modification of extraction procedures to achieve simplicity, sensitivity, and speed. Recently, the extraction procedures based on supramolecular solvents has been applied (18-20). This method depends on the combination of dispersion behavior and hydrogen bonding which leads to a quick phase separation with high recov-

ery of the metal ions in the presence of a suitable complexing agent (20). N-Benzoyl-N,N-diisobutylthiourea is a commonly used ligand to chelate heavy metal ions, but until now and according to our literature study, it was not used for supramolecular molecular extraction of copper.

The goal of this work was to develop supramolecular extraction procedures using a shorter time and simple operating steps for copper preconcentration with N-Benzoyl-N,N-diisobutylthiourea as the complexing agent. The process was controlled by optimizing the pH of the copper sample solution, the amount of organic chelate, and the effect of the coexisting ions.

EXPERIMENTAL

Instrumentation

A PerkinElmer® Model 3110 flame atomic absorption spectrometer (FAAS) (PerkinElmer, Inc., Shelton, CT, USA), equipped with a copper hollow cathode lamp and air-acetylene flame, was used for the absorbance measurements. The instrumental operating conditions are listed in Table I.

TABLE I
Instrumental Operating
Conditions for FAAS
Determination of Cu

Instrument	PerkinElmer Model 3110 FAAS
Wavelength	324.8 nm
Slit width	0.7 nm
Lamp current	15 mA

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The samples were injected into the FAAS using a micro-injection system, which consists of a mini home-made Teflon® funnel with an Eppendorf® pipette. The peak heights were recorded as signals. A Nel pH-900 pH meter (Ankara, Turkey) with a combined glass electrode was used for the pH measurements. An ALC PK 120 Model centrifuge (Buckinghamshire, England) was also used.

Reagents and Solutions

The chemicals applied in this work were high purity and of analytical grade. All solutions were prepared with deionized water using a Millipore® Milli-Q® system (Millipore Corporation, USA). The Cu(II) standard solutions (1000 mg L⁻¹) were prepared by dissolving the nitrate salt (E-Merck, Darmstadt, Germany) in water. The daily working standard solutions were obtained by dilution of the stock standard solutions.

Extraction Procedures

For optimization of the supramolecular extraction procedure, 20 mL ultrapure water containing 20 µg copper(II) was added into a 50-mL centrifuge tube, together with a 3-mL amount of phosphate buffer, and the pH adjusted to 3. Then, 100 µL of 0.01% N-Benzoyl-N,N-diisobutylthiourea was added for Cu(II) chelation. Next, a mixture of tetrahydrofuran (100 µL) and 1-decanol (50 µL) was injected to this solution resulting in the formation of the supramolecular solvent. The mixture was exposed to ultrasonic waves for 3 to 5 minutes, and then vigorously shaken on the vortex for 1 minute. Finally, the phase was separated by centrifugation at 4000 rpm for 10 minutes, and the aqueous phase separated by suction. The isolated supramolecular solvent, including the Cu(II), was dissolved in ethanol, brought to a final volume of 500 µL and

then 50 µL of final solution was injected into the FAAS.

Water samples, including wastewater, seawater, dam water, valley water, and mineral water were collected from various regions in Turkey. The samples were transferred to the laboratory in polyethylene bottles, filtered with a Millipore® cellulose membrane filter of 0.45-micrometer pore size. All of these samples were treated according to the supramolecular microextraction procedure described above before the determination of copper. In addition, the procedure was applied to certified reference materials (CRMs) TMDA 64.2 and TMDA 53.3 Fortified Water (National Water Research Institute, Environment Canada, Burlington, Canada).

RESULTS AND DISCUSSION

Optimization of Cu(II) Complexation and Extraction by Supramolecular Technique

Experiments were conducted to evaluate the effect of pH of the Cu(II) solution, amount of N-Benzoyl-N,N-diisobutylthiourea chelating agent, the composition of the supramolecular solvent, the effect of different matrix, and the initial sample volume. The (%) recovery was calculated in each case from Equation 1 as follows:

Eq. (1)

$$\text{Recovery}(\%) = \frac{\text{Recovered Cu(II) concentration}}{\text{Initial Cu(II) concentration}} \times 100 \quad (1)$$

The pH of the sample solution significantly affects the chelation with the N-Benzoyl-N,N-diisobutylthiourea ligand and, therefore, controls the transferring process of Cu(II) from the aqueous solution to the supramolecular solvent (18-20). To maximize the (%) recovery, investigation of the pH effect is necessary. The pH of the Cu(II) sample solution was studied from 2 to 8 and the resultant (%) recovery is presented in Figure 1. This shows that maximum recovery was at pH 3, and was thus chosen for further studies.

The developed supraextraction procedure is based on the isolation of Cu(II) after complexing with N-Benzoyl-N,N-diisobutylthiourea. Therefore, the amount of N-Benzoyl-N,N-diisobutylthiourea ligand is a key factor for best performance and quantitative recovery of the process. In this work, different amounts of N-Benzoyl-N,N-diisobutylthiourea ligand were evaluated, and the (%) recovery is shown in Figure 2. This indicates that 100 µL is suitable to chelate the existing Cu(II) amount and leads to quantitative recovery.

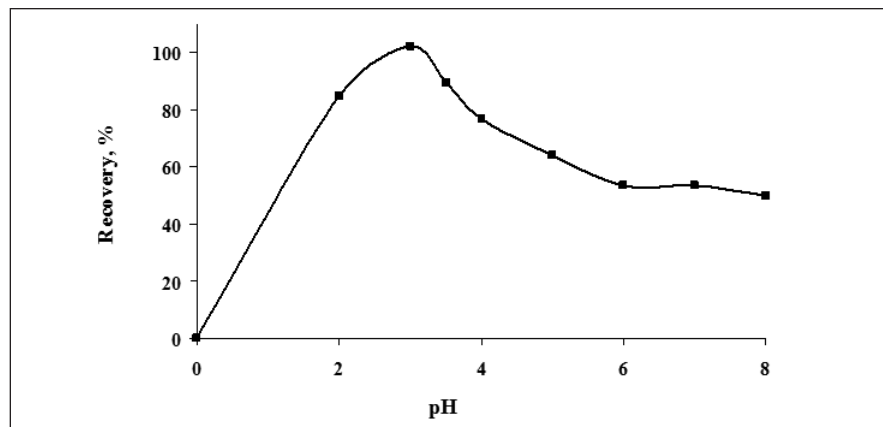


Fig. 1. Effect of pH on the recovery (%) of Cu(II) (N=3).

Different combinations of the supramolecular solvent were evaluated including tetrahydrofuran with 1-decanol, tetrahydrofuran with undecanol, and tetrahydrofuran with decanoic acid (18, 20), and the (%) recovery was calculated. It was found that the recovery was 100%, 63%, and 51%, respectively. Furthermore, the effect of increas-

ing the amount of tetrahydrofuran at constant 1-decanol (Figure 3a), the effect of changing the volume of 1-decanol at constant tetrahydrofuran (Figure 3b), as well as the ratio between tetrahydrofuran and 1-decanol (Figure 3c) were investigated. It is clear from the graphs that 100 μL of tetrahydrofuran and 50 μL of 1-decanol are necessary to

achieve quantitative recoveries. The ratio between tetrahydrofuran and 1-decanol for quantitative recoveries was found to be at the ratios of 0.5, 5.3, 8, and 16.

The time of exposure to the ultrasonic procedure was evaluated to assess the formation of the supramolecular solvent and to enhance the transference of the complexed copper ions to the organic phase. The results presented in Figure 4 show that the exposure time between 3 to 5 minutes was suitable for quantitative recovery. After 5 sanitation minutes, the recoveries of copper decreased and were not quantitative due to corruption of the copper chelates with excess ultrasonic waves.

According to the literature, the presence of coexisting ions may interfere in the extraction procedure (21-30). To ensure the effectiveness of the developed supramolecular microextraction proce-

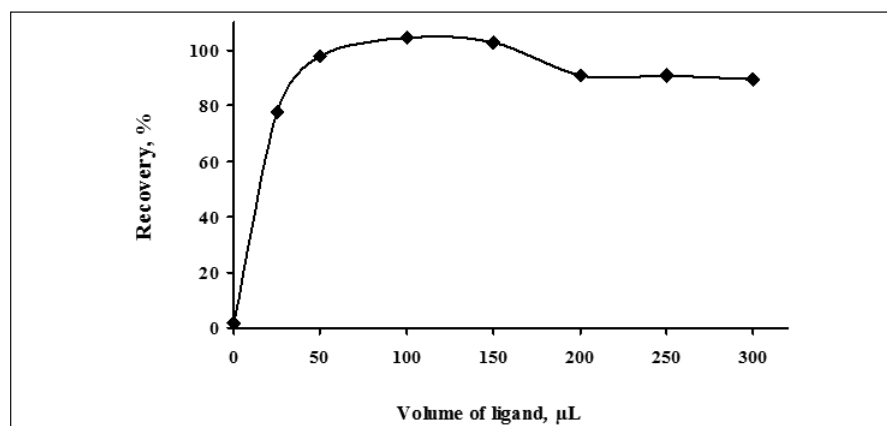


Fig. 2. Effect of the quantity of *N*-Benzoyl-*N,N*-diisobutylthiourea on the recovery of Cu(II) ($N=3$).

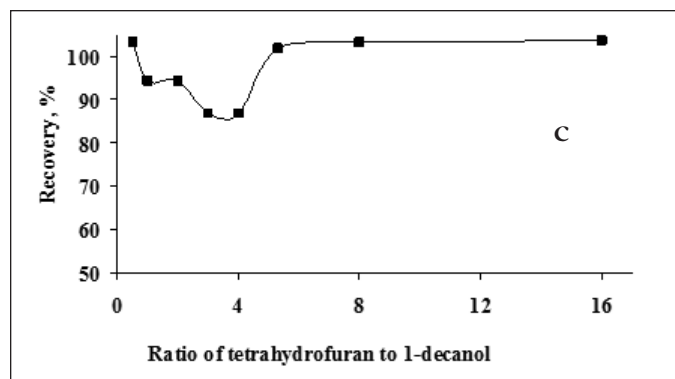
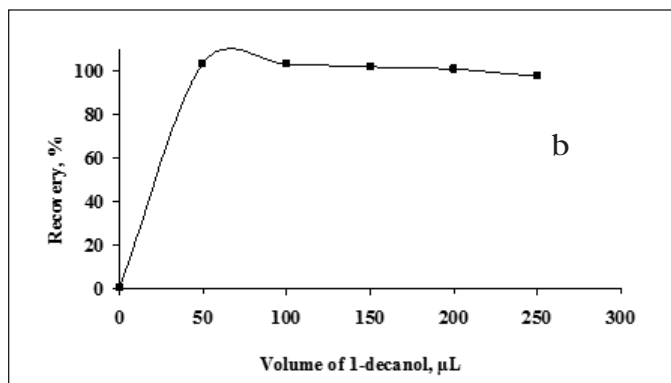
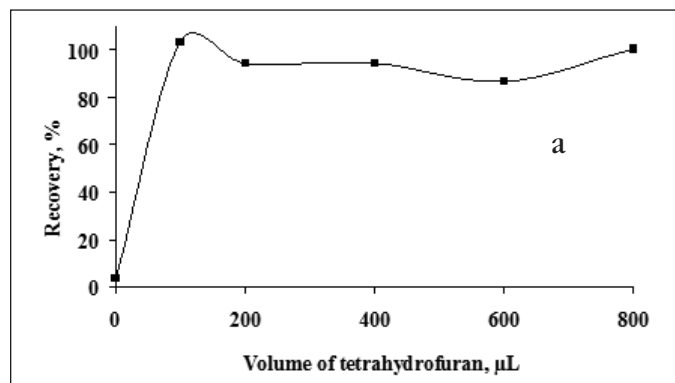


Fig. 3 (a, b, c). Effect of the composition of supramolecular solvent on the recovery of Cu(II) ($N=3$).

ture, the effect of the presence of F^- , Cd^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Zn^{2+} , CO_3^{2-} , NO_3^- , K^+ , Cl^- , Mg^{2+} , Ca^{2+} , SO_4^{2-} and Na^+ was evaluated. Table II lists the recovery, in % for each case. The results indicate that the proposed microextraction method is applicable for all tested ions.

It was found that the initial volume of the Cu(II) sample solution controls the preconcentration factor of the developed supramolecular procedure. It is usually calculated as the ratio between the initial Cu(II) sample volume and the

last volume after extraction (31-39). It was investigated what happened when the initial Cu(II) sample solution volume was changed from 10 mL to 50 mL. Figure 5 shows that quantitative (%) recovery was obtained with a sample volume up to 45 mL, resulting in a preconcentration factor of 90 considering that the last volume was 0.5 mL.

Analytical Features

The detection limit (LOD) of the presented method, calculated based on 11 determinations of the standard deviation of the blank,

was $0.46 \mu g L^{-1}$. The relative standard deviation (RSD) determined from 11 analyses of the Cu(II) standard solution ($0.1 mg L^{-1}$) was 3.3%.

Applications

The accuracy of the method was evaluated by spiking a natural water sample with a certain concentration of Cu(II), then applying the developed supramolecular extraction procedures. The results in Table III show that the developed procedure is applicable for the different concentrations of Cu(II). In addition, for the CRMs TMDA 64.2 and TMDA 53.3 Fortified Water samples analyzed and using the proposed method, the recoveries were calculated. Table IV lists the obtained (%) recoveries which are in agreement with the values of the certified reference materials.

TABLE III
Addition-Recovery Tests for the Present Procedure for Cu(II) From a Water Sample (N=3)

Added (μg)	Found (μg)	Recovery (%)
0	0	-
1.5	1.5 ± 0.5	100
3.0	3.1 ± 0.3	103

TABLE II
Effect of Some Coexisting Ions on the Recovery of Cu(II) (N=3)

Ions	Concentration (mg/L)	Added As	Recovery (%)
F^-	250	NaF	91 ± 5
Cd^{2+}	20	$Cd(NO_3)_2 \cdot 6H_2O$	95 ± 3
Ni^{2+}	20	$Ni(NO_3)_2 \cdot 6H_2O$	92 ± 4
Co^{2+}	20	$Co(NO_3)_2$	96 ± 3
Fe^{2+}	20	$Fe(NO_3)_3 \cdot 9H_2O$	96 ± 3
Zn^{2+}	10	$Zn(NO_3)_2$	95 ± 3
CO_3^{2-}	800	Na_2CO_3	97 ± 1
NO_3^-	400	KNO_3	91 ± 5
K^+/Cl^-	1000	KCl	91 ± 5
Mg^{2+}	200	$Mg(NO_3)_2 \cdot 6H_2O$	90 ± 4
Ca^{2+}	200	$CaCl_2$	90 ± 3
SO_4^{2-}	500	Na_2SO_4	92 ± 5
Na^+	10000	NaCl	97 ± 3

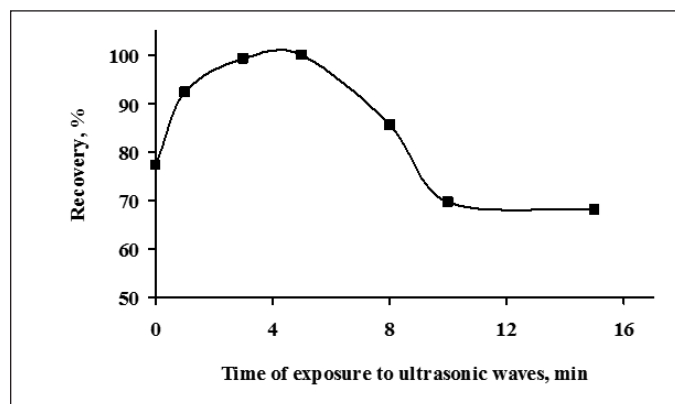


Fig. 4. Effect of exposure to ultrasonic waves on the recovery of Cu(II) (N=3).

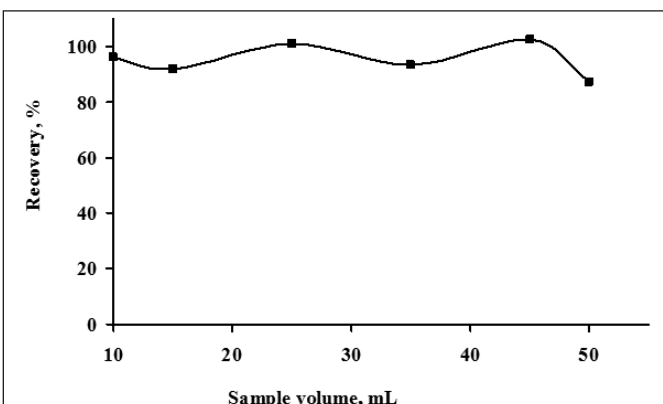


Fig. 5. Effect of sample volume on the recovery of Cu(II) (N=3).

Different types of water samples from Turkey were analyzed using the developed supramolecular-based microextraction procedures. The results in Table V show that the proposed procedure is applicable to the microextraction of copper from various water samples.

A comparison of the results of the proposed supramolecular-based microextraction procedure for copper preconcentration with other methods is provided in Table VI (18, 40-43). It can be seen that the proposed method is effective for Cu determination in real samples.

CONCLUSION

The supramolecular solvent of tetrahydrofuran with 1-decanol was applied for the development of an effective supramolecular extraction procedure in the FAAS determination of Cu(II) in water samples from different regions in Turkey. Quantitative (%) recovery was obtained using a weak acidic medium in the presence of N-Benzoyl-N,N-diisobutylthiourea as the ligand. The extraction procedure is applicable for different sample volumes up to 45 mL. The preconcentration factor obtained was 90, the limit of detection $0.46 \mu\text{g L}^{-1}$, and the RSD was 3.3%. The proposed method was verified by applying it to the analysis of CRMs TMDA 64.2 and TMDA 53.3 Fortified Water. It can be seen from the results that the presented procedure is simple and ecofriendly and is applicable for saline sample analysis from the environment.

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TABLE IV
Application of Present Procedure to CRMs (N=3)

	Certified Value ($\mu\text{g L}^{-1}$)	Found Value ($\mu\text{g L}^{-1}$)	Recovery (%)
TMDA 64.2	274	272 ± 1	99.3
TMDA 53.3	308	313 ± 1	101.6

TABLE V
Application of Present Procedure for Determination of Cu in Water Samples (N=3)

Samples	Concentration ($\mu\text{g L}^{-1}$)
Wastewater	97.5 ± 1.2
Sea water	73.8 ± 1.1
Dam water	59.0 ± 0.5
Valley water	39.3 ± 0.6
Mineral water	32.4 ± 0.6

Mean $\pm$ standard deviation.

TABLE VI
Comparison Between Present Procedure and Other Methods From Literature

Method	LOD ($\mu\text{g L}^{-1}$)	Ref.
Dispersive liquid-liquid microextraction (DLLME)	7.9	(6)
Dispersive liquid-liquid microextraction (DLLME)	1.4	(9)
Dispersive liquid-liquid microextraction (DLLME)	2.54	(10)
Solid Phase Extraction (SPE)	0.2	(11)
Solid Phase Extraction (SPE)	0.06	(13)
Cloud Point Extraction (CPE)	0.48	(15)
Dispersive liquid-liquid microextraction (DLLME)	0.75	(16)
Dispersive liquid-liquid microextraction (DLLME)	0.19	(23)
Supramolecular microextraction (SME)	0.46	This study

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