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Development a novel supramolecular solvent microextraction procedure for copper in environmental samples and its determination by microsampling flame atomic absorption spectrometry[☆]

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ABSTRACT

A supramolecular solvent (Ss) made up of reverse micelles of 1-decanol in tetrahydrofuran (THF): water was used for the fast and selective microextraction of Cu(II) prior to its determination by microsampling flame atomic absorption spectrometry (FAAS). Cu(II) was complexed with dimethyl dithiocarbamate (DMDC) to obtain hydrophobic complex and extracted to supramolecular solvent phase. The influences of some analytical parameters including pH, type and volume of supramolecular solvent, amount of complexing agent, ultrasonication and centrifuge time and sample volume were investigated. The effects of matrix components were also examined. The detection limit (LOD) and the quantification limit (LOQ) were 0.52 $\mu g\ L^{-1}$ and 1.71 $\mu g\ L^{-1}$ respectively. An preconcentration factor was obtained as 60 and the relative standard deviation was $<3\%$. The accuracy of the developed method was evaluated by the analysis of the certified reference materials (TMDA-64.2 water, SRM 1568 A Rice Flour and 8433 Corn Bran) and addition-recovery tests. The presented supramolecular solvent based liquid–liquid microextraction (SsLLME) procedure was applied to the determination of copper in food and water samples with satisfactory results.

1. Introduction

Copper is an important and essential element for biological systems. But, the ingestion or inhalation of large doses of copper may lead to toxic effects [1–6]. Hence, the accurate, precise and fast determination of trace level of copper in real samples becomes important [7]. The determination of copper at ultratrace levels by flame atomic absorption spectrometry is difficult because of the low concentration of its and effects of the matrix components in environmental and food samples [7,8]. To overcome these limitations on the determination of trace amounts of copper and other elements by flame atomic absorption spectrometry, separation-enrichment techniques are frequently required to achieve accurate, reliable and sensitive results [9–12].

Up to now, many classical sample preparation method including solid phase extraction (SPE) [13,14], liquid–liquid extraction (LLE) [15,16] and cloud point extraction (CPE) [17,18] have been developed. However these methods are time-consuming, tedious and use large amounts of high purity solvents which are expensive, toxic and contaminant for the environment due to their high vapor pressure. In order to remove these disadvantages, the microextraction techniques like liquid phase microextraction (LPME) and solid phase microextraction (SPME) were developed [19–21].

In recent years, supramolecular solvent-based microextraction (SsSME) has been developed as an environment friendly alternative method to other microextraction technique for determination of organic and inorganic species [22–30]. The supramolecular solvents have the capability to provide different type of interactions (e.g. hydrophobic and hydrogen bonding) with the organic compound and hydrophobic complex of metals with ligand. The interactions are important for extraction of analytes from water phase to supramolecular solvent phase and for increase extraction efficiency [22,23]. The supramolecular assemblies provide unique properties like high extraction capability and short extraction time (extractions are performed in a few minutes), low cost, simple preparation at room temperature using conventional laboratory conditions, and solubilization of analytes in supramolecular systems [22–28].

In this study, the suitability of supramolecular solvent based liquid–liquid microextraction technique (SsLLME) for the separation and preconcentration of copper in real samples prior to its micro sampling-flame atomic absorption spectrometric determinations was explored.

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2. Experimental

2.1. Apparatus

Absorbance measurements were performed using a Perkin-Elmer Model 3110 model flame atomic absorption spectrometer (Norwalk, CT, USA) (FAAS) including air–acetylene flame and a hollow cathode lamp. The instrumental parameters were adjusted as follows: wavelength 324.8 nm, slit width: 0.7 nm and lamp current: 15.0 mA. The continuous aspiration mode was used to measure the copper ions concentration in extractant phase diluted with methanol. 100 μL of the diluted phase was taken and injected into the FAAS nebulizer by using a home-made microsample introduction system consist of Teflon funnel and Eppendorf pipette and the peak height was measured [31]. For pH adjustments, Sartorius PT-10 pH meter (Germany) with glass-electrode was used. An ultrasonic water bath (Sonorex, DT-255, Berlin, Germany) was used for supramolecular solvent production. A centrifuge (ALC PK 120 Model, Buckinghamshire, England) was used for phase separation.

2.2. Reagents and solutions

Ultra pure water purified through reverse osmosis (18.2 MΩ cm, Millipore) was used for solutions preparation. All chemicals were analytical reagent grade and were used as supplied. Working standard solutions were prepared by appropriate dilution of the stock solution with water. Extraction solvents (1-Decanol, Undecanol) were obtained from Merck (Darmstadt, Germany). Decanoic acid was obtained from Sigma-Aldrich (St. Loius, MO, USA). THF was obtained from Merck (Darmstadt, Germany). Concentrated 30% (v/v) H_2O_2 (Darmstadt, Germany) and 65% HNO_3 (Darmstadt, Germany) were used for digestion of food samples and the certified reference materials (SRM 1568 A Rice Flour, 8433 Corn Bran and TMDA-64.2 Water-Trace Elements).

A 0.1% (w/v) sodium dimethyl dithiocarbamate (DMDC) which obtained from Sigma-Aldrich (St. Loius, MO, USA) was daily prepared in ethanol. The phosphate buffer solutions for pH 2.0–4.0, acetate buffer solution for pH 5.0, phosphate buffer for pH 6.0–7.0 and ammonium/ammonia buffer solutions for pH 8 were prepared and used to adjust of pH of sample solutions.

2.3. Supramolecular solvent based liquid–liquid microextraction procedure

10 mL of an aqueous solution containing 0.25 μg of Cu(II), 0.2 mg dimethyl dithiocarbamate and 2.0 mL of 1.0 mol L^{-1} buffer solution (pH 6.0) was transferred to a 50 mL conical-bottom glass centrifuge tube. Then, 525 μL of extraction solution consist of 1-decanol (125 μL) and THF (400 μL) was injected in to the sample solution and the mixture was kept in an ultrasonic bath for 5 min. The supramolecular solvent spontaneously formed into the bulk solution and then the solution was centrifuged at 4000 rpm for 6 min to accelerate the complete separation of the two immiscible liquids. The supramolecular solvent on the surface of the aqueous solution due to its lower density than water was obtained. The upper supramolecular solvent phase (approximately 100–150 μL) was taken with micropipette and its volume completed to 250 μL with methanol. Finally, 100 μL of the preconcentrated solution phase was introduced to the nebulizer of the FAAS using a home made microinjection system in continuous aspiration mode for measurement.

2.4. Pre-treatment of samples

The food samples and mineral water samples were collected from local store in Kayseri. The food samples were dried at temperature 80 °C for 24 and homogenized with an agate homogenizer. The solid certified reference materials (0.15 mg) and food samples (0.25 mg) were accurately weighted into beakers, covered with a watch glass and digested with 10 mL concentrated HNO_3 at 100 °C. The mixtures were evaporated almost to dryness and were again digested with 5 mL of concentrated H_2O_2 and 10 mL concentrated HNO_3 at 100 °C. Then it was evaporated to near dryness. The residues obtained were dissolved in about 5 mL distilled water, completed to 10 mL and the supramolecular solvent based liquid–liquid microextraction (SsLLME) procedure was applied to the samples. The mineral water samples were heated at temperature 80 °C to remove carbon dioxide at 2 h. Then the SsLLME procedure was applied to the samples.

3. Results and discussion

3.1. Effect of pH

The pH of the sample solution is one of the most important factors in supramolecular solvent microextraction for the formation of the supramolecular solvent and for extraction of hydrophobic metal–ligand complex [27–30]. The results shown in Fig. 1 indicate that the quantitative extraction efficiency for Cu(II) ions can be achieved when the pH of sample solution was adjust at 6.0. Therefore, pH 6.0 was selected for the further study.

3.2. Effect of the type of supramolecular solvent

To select the best supramolecular extraction solvent, three supramolecular solvent including; 1-decanol–THF, undecanol-THF and decanoic acid-THF were tested. The recovery% values of copper(II) with 1-decanol-THF, undecanol-THF and decanoic acid-THF were 100 ± 0, 72 ± 5 and 75 ± 2, respectively. Hence, 1-decanol-THF supramolecular solvent was used for the further study.

3.3. Effect of the volume ratio of 1-decanol and THF

The composition and volume of the supramolecular solvent have key role greatly affecting its extraction capability [27,28]. The supramolecular solvent used was prepared 1-decanol reverse micelles dispersed in a THF:water continuous phase. The influence of varying the 1-decanol/THF volume ratio on the extraction

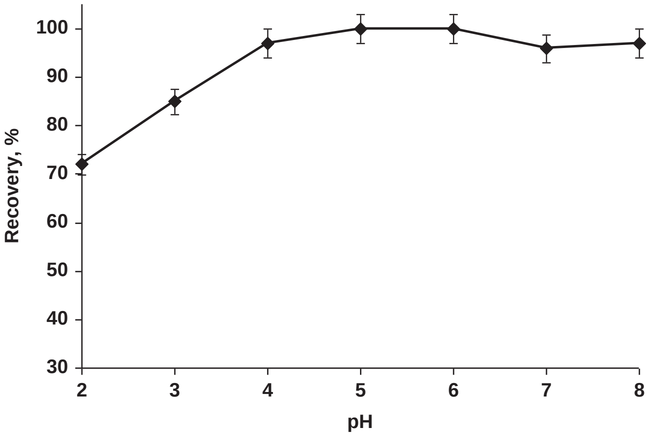

Fig. 1. Effect of the pH on the recovery of Cu(II) (N=3).

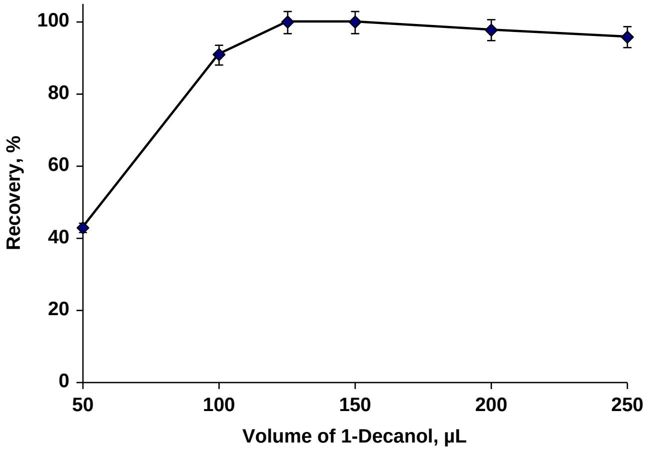

Fig. 2. Effect of the volume of 1-decanol on the recovery of Cu(II) (*N*=3).

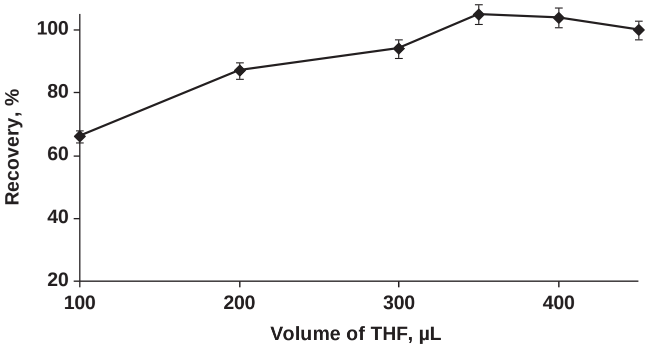

Fig. 3. Effect of the volume of THF on the recovery of Cu(II) (*N*=3).

efficiency of copper was examined in the range 0.125–0.625 For this purpose, a set of experiments was performed using different 1-decanol volumes (50–250 µL) and while the volume of THF was fixed as 400 µL. The results were given in Fig. 2. 125 µL volume of 1–decanol was adequate for quantitative extraction of Cu–DMDC complex.

After selection of the optimum volume of 1-decanol, the volume of THF was examined by varying from 100 to 450 µL. The quantitative results were obtained between 350 and 450 µL (Fig. 3). 400 µL of THF was selected as optimum value. The results shown in Figs. 2 and 3 indicate that higher extraction efficiency for Cu(II)–DMDC can be achieved when the 1-decanol/THF volume ratio was set at 0.313.

3.4. *Effect of the amount of DMDC*

In order to obtain hydrophobic copper complex, DMDC was selected as ligand and the influence of its amount on the recovery was examined by varying amounts of 0.0–0.5 mg. The results are depicted in Fig. 4. The quantitative recovery values were obtained for Cu(II) in the presented system in the range of 0.1–0.5 mg of ligand. 0.2 mg of DMDC was selected as optimum value.

3.5. *Effect of ultrasonication and centrifuge time*

As is known, analytical application of ultrasonic radiation has an important role in increasing the kinetics and performance of extraction by increasing the interactions between analyte and extraction solution for mass transfer [32,33]. Hence, after addition of the extraction solvent (1-decanol–THF) in sample solutions, the sample solutions were placed in ultrasonic water bath. The supramolecular solvent, made up of reverse micelles of 1-decanol dispersed in THF:water formed. Linear increase in recovery was obtained as ultrasonication time was increased up to 5 min. which was enough for maximum recovery. Hence, 5.0 min. of ultrasonicaiton time was used for further work.

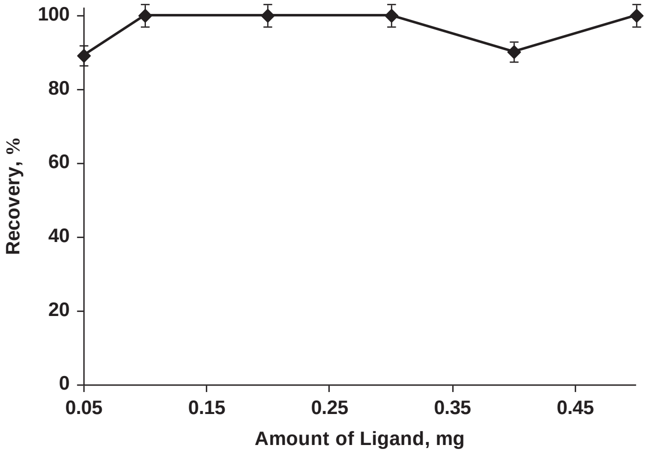

Fig. 4. Effect of the amount of dimethyl dithiocarbamate on the recovery of Cu(II) (*N*=3).

Table 1
Effect of some matrix ions on the extraction efficiency of Cu(II) (*N*=3).

Ion	Added as	Concentration (mg/L)	Recovery (%)
Na^+	$NaNO_3$	2500	103 ± 1
K^+	KCl	2500	98 ± 1
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	2000	100 ± 3
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	2000	100 ± 0
Zn^{2+}	$Zn(NO_3)_2 \cdot 6H_2O$	20	97 ± 1
Mn^{2+}	$Mn(NO_3)_2 \cdot 4H_2O$	20	95 ± 3
Cr^{3+}	$Cr(NO_3)_3 \cdot 9H_2O$	20	102 ± 6
Fe^{3+}	$Fe(NO_3)_3 \cdot 9H_2O$	10	100 ± 4
Cd^{2+}	$Cd(NO_3)_2 \cdot 4H_2O$	20	102 ± 3
Cl^-	KCl	2500	98 ± 1
SO_4^{2-}	Na_2SO_4	2000	101 ± 1

Table 2
The analysis results for certified reference materials (*N*: 5).

Certified Reference Materials	Certified value	Found	Recovery (%)
TMDA-64.2 Water - Trace Elements (µg L^{-1})	274	278 ± 8[a]	101
SRM 1568A Rice Flour (µg g^{-1})	2.4	2.3 ± 0.2	96
8433 Corn Bran (µg g^{-1})	2.4 ± 0.1	2.4 ± 0.1	100

[a] Mean ± standard deviation.

The effects of centrifugation time on the recovery of Cu(II) in the presented system were checked at 4000 rpm between 2 and 6 min. The quantitative recovery was obtained with 6 min of centrifuge time.

3.6. *Effect of matrix*

The matrix ions at high concentrations have influence on atomic absorption spectrometric determination of metals at trace levels [31,34]. The study was performed by analyzing 10 mL of 25 µg L^{-1} of copper(II) solution containing matrix ions at different concentrations. The matrix ions listed in Table 1 were added to the model solutions under the optimized conditions and check using the proposed method. According to the obtained results in Table 1,

Table 3
Addition/Recovery of copper(II) from mineral water and food samples ($N=5$).

Plain mineral water			**Mixed flavored mineral water**			**Apple flavored mineral water**		
Added µg	**Found (µg)**	**Recovery (%)**	**Added (µg)**	**Found (µg)**	**Recovery (%)**	**Added (µg)**	**Found (µg)**	**Recovery (%)**
0.0	0.04 ± 0.00[a]	–	0.0	0.07 ± 0.004	–	0.0	[b]BDL	–
0.1	0.14 ± 0.01	100	0.1	0.17 ± 0.03	100	0.1	0.10 ± 0.01	100
0.25	0.29 ± 0.02	100	0.25	0.30 ± 0.02	94	0.5	0.51 ± 0.02	102
0.50	0.52 ± 0.003	96	0.5	0.57 ± 0.02	100	1.0	1.02 ± 0.05	102
Cracked wheat			**Chili powder**			**Black Pepper**		
Added µg	**Found (µg)**	**Recovery (%)**	**Added (µg)**	**Found (µg)**	**Recovery (%)**	**Added (µg)**	**Found (µg)**	**Recovery (%)**
0.0	0.29 ± 0.004	–	0.0	1.18 ± 0.06	–	0.0	1.82 ± 0.04	–
0.25	0.55 ± 0.04	102	0.5	1.68 ± 0.13	100	0.5	2.38 ± 0.08	103
0.50	0.77 ± 0.02	97	1.0	2.16 ± 0.02	99	1.0	2.85 ± 0.12	101

[a] Mean ± standard deviation.
[b] BDL: below of the detection limit.

Table 4
Determinations of Cu (II) in food samples by using presented method ($N=5$).

Sample	**Concentration (µg/L)**
Strawberry flavored mineral water	15 ± 0.2[a]
Watermelon–strawberry mixed mineral water	9 ± 0.1
Pomegranate mineral water	14 ± 0.1
	Concentration (µg/g)
Noodles	2.0 ± 0.2
Dried beans	3.7 ± 0.2
Chick pea	5.8 ± 0.1
Red lentils	4.5 ± 0.1

[a] Mean ± standard deviation.

Table 5
Comparisons between the analytical performances of presented method for Cu(II) with different preconcentration procedures combined with flame atomic absorption spectrometry.

Method	PF[a]	LOD[b] (µg L^{-1})	RSD[c] (%)	References
Dispersive liquid–liquid microextraction	136.6	0.45	3.3	20
Ultrasound-assisted ionic liquid based dispersive liquid–liquid microextraction	56	1.9	3.8	35
Hollow fiber supported liquid membrane microextraction	551	4	6	36
Solid phase extraction	41	0.56	1.6	37
Flow injection cloud point extraction	99	0.57	2.3	38
Dispersive liquid–liquid microextraction	48	3	5.1	39
Supramolecular solvent based liquid–liquid microextraction	60	0.52	2.6	This work

[a] Preconcentration factor.
[b] Limit of detection.
[c] Relative standard deviation.

the major ions in real samples have no significant influence on the determination of copper.

3.7. *Effect of the sample volume*

The effect of sample volume on the extraction efficiency was also examined by using model solutions prepared in the range of 10–40 mL and keeping other conditions constant. When the volume of sample was greater than 15 mL, the recovery of Cu(II) ions was not quantitative. Therefore, 15 mL was selected as the greatest working sample volume. The calculated preconcentration factor was 60 when the final volume was 0.25 mL.

3.8. *Analytical features*

The equation of a typical calibration line was $A=0.0017C+0.0024$ with a correlation coefficient ($R^2=0.989$), where A is the absorbance and C is the copper concentration in solution (µg L^{-1}). The enhancement factor (EF) calculated as the ratio of the slope of calibration curve of the copper (II) after preconcentration to that of prior preconcentration was found as 53. The limit of detection, LOD, was calculated as the ratio of three times standard deviation of ten blank absorbances to the slope of the calibration curve was 0.52 µg L^{-1}, where the limit of quantification, LOQ, was found as the ratio of ten times the standard deviation of the ten blank solution to the slope of the calibration curve was 1.71 µg L^{-1}. The precision of the presented method was given as relative standard deviation (RSD) which evaluated for seven successive supramolecular solvent microextraction of 25 µg L^{-1} of copper (II) was 2.6%.

In order to validate the developed method, the method was applied for determination of copper in the SRM 1568A Rice Flour, 8433 Corn Bran and TMDA-64.2 water–trace elements certified reference materials. Comparison of the copper concentration found with the certified value show good accuracy of the method (Table 2). Furthermore, the accuracy of the developed method was evaluated by applying the addition and recovery experiments for water and food samples. The recovery results given in Table 3 show that a good agreement was obtained between the added and recovered copper contents. The proposed procedure was reliable and independence from matrix effects for determination of wide range of samples.

3.9. *Application of the method*

The proposed method was used for determination of copper concentration in various mineral water and food samples obtained from market in Kayseri, Turkey. The results are given in Table 4.

3.10. *Comparison with other preconcentration techniques*

The presented SsLLME method was compared with the other preconcentration methods combined with flame atomic absorption spectrometer used for the determination of copper in real samples (Table 5). The proposed method has generally low LOD, good relative standard deviation and preconcentration factor with some exceptions. It is comparable with some procedures described in the literature [20,35–41].

4. Conclusion

A novel and simple supramolecular solvent based liquid–liquid microextraction technique (SsLLME) combined with FAAS is described for the determination of Cu(II) in food and water samples without matrix interferences. Copper was quantitatively recovered at pH 6.0 with 1-decanol–THF supramolecular solvent. It shows low detection limit (0.52 $\mu g\ L^{-1}$) with a sample volume of only 15 mL and has quantitative recoveries (> 95%), preconcentration factor (60) and good repeatability within 5 min.

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