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 micro-extraction (SsLLME) procedure was applied to the determination of copper in food and water samples with satisfactory results.

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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.

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
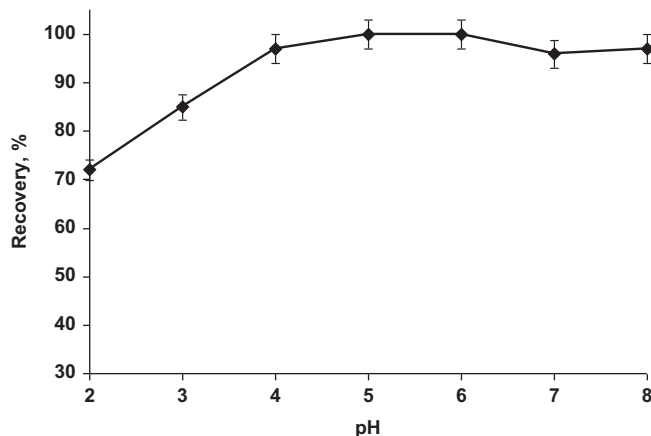

Fig. 1. Effect of the pH on the recovery of Cu(II) ($N=3$).