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Solid Phase Extraction of Trace Copper in Aqueous Samples Using C_{18} Membrane Disks Modified by Benzildithiosemicarbazone Prior to Flame Atomic Absorption Spectrometric (FAAS) Determination

*M. Mohammadhosseini**

Department of Chemistry, Faculty of Basic Sciences, Shahrood Branch, Islamic Azad University, Shahrood, Iran

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Abstract: A highly convenient, selective and sensitive procedure for pre-concentration, separation and determination of sub-ppm levels of Cu^{2+} in aqueous samples based on modification of octadecyl silica bonded phase membrane (OSBPM) disks is described using benzildithiosemicarbazone (BDSC) as a powerful modifier. It was revealed that each loaded OSBPM disk with 6.0 mg of BDSC serves as excellent bead for trapping, enrichment and isolation of trace copper. The analyte was trapped during introduction the aqueous solutions through the surface of each modified membrane, quantitatively, while other interfering ions passed through the disk to drain. The adsorbed Cu^{2+} ions were then stripped by appropriate eluting agents followed by monitoring of the eluates by FAAS. The effects of sample pH, amount of the modifier, stripping agent types and sample flow-rates were also investigated. The described method permitted a pre-concentration factor of about 200. The detection limit of the procedure was predicted to be about 0.013 ng L^{-1}. The method was successfully employed for recovery and quantification of trace copper in different water samples.

Keywords: benzildithiosemicarbazone (BDSC), FAAS , Cu^{2+}, pre-concentration

INTRODUCTION

Copper is one of the most abundant elements occurring in a wide variety of samples. The sub-ppm levels of copper are required for performance of the vital activities in the human body while its great contents results in malfunctions in the metabolisms and noxious side effects [1].

Solid phase extraction is one the most common used strategies to concentrate trace heavy metals present in most of the real samples before their measurement. Many reports are found in the literature concerning the use of OSBPM disks among them some relate to our research group [2-7] .These methods are different from each other mainly by type of employed modifier involved in each case. In the present work, a reliable method has been established for rapid separation of trace copper from its initial matrix by using OSBPM disks and subsequent analysis by FAAS.

EXPERIMENTAL

Reagents and materials

All chemicals were of analytical reagent grade (E.Merck, Darmstadt, Germany), and used as received without any further purification except for vacuum drying over P_2O_5. A 0.1 mol L^{-1} acetic acid-sodium acetate buffer was prepared by dissolving appropriate amounts in 500 mL water, then

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Corresponding Author: *M. Mohammadhosseini***,** Department of Chemistry, Faculty of Basic Sciences, Shahrood Branch, Islamic Azad University, Shahrood, Iran. Email: mohammadhosseini_iri@yahoo.com

adjusting the pH to 4 with sodium hydroxide solution and diluting to a volume of 1000 mL with water.

Apparatus

Determination of copper in working samples was carried out on a Varian spectra A.200 model atomic absorption spectrometer equipped with a copper high intensity hallow cathode lamp (HI-HCL) under the recommendations of the manufacturers. An ICP-AES JY 138 Ultrace was also used to confirm the reliability of the method.

Synthesis of Benzildithiosemicarbazone

Benzildithiosemicarbazone (BDSC) was synthesized and recrystallized as previously reported in the literature [8]. The method was based on the addition of 3 cm^3 of concentrated hydrochloric acid to a refluxing mixture containing 50 cm^3 of methanolic benzil (0.420 g) and 50 cm^3 of aqueous thiosemicarbazide (0.365 g) solutions. The reaction mixture was then kept on a hot water bath for about 30 min. A light yellow colored product was obtained which was separated by filtration followed by its complete drying. Finally, the product was re-crystallized from ethanol. Ascertaining the melting point and elemental analysis checked the purity of the reagent.

Sequential SPE steps

Preliminary step

Solid phase extractions were carried out by OSBPM disks, Empore 47 mm diameter × 0.6 mm thickness containing octadecyl silica bonded phase (irregular 8 μm particles, 6 nm pore size) distributed by 3M company St. Paul, MN. To remove potential interferences and to ensure optimal extraction of the analyte(s) of interest, 10 mL portions of methanol and triple distilled water were poured onto the disk, and immediately drawn through the disk by applying a low vacuum. When all the solvent passed though the disk, it was dried by passing air through it for two minutes.

Disk conditioning and its impregnation

This step was conducted by pouring 10 mL portions of HPLC grade methanol onto the disk under a low vacuum followed by the solvent passage through the disk until the solvent surface almost reaches the surface of the disk. The disk should not be allowed to soak without vacuum and air contact with the surface of the disk should be avoided. This is to ensure complete wetting of the disk with the organic solvent. Then, 20 mL of water was poured onto the disk and was drawn through it followed by again drying of the disk. In the next step, a solution of 6.0 mg of BDSC in 4.0 mL of DMSO was introduced onto the disk and drawn slowly through it under a mild vacuum. The passed solution was collected in a test tube. Then, water was added drop-by-drop to the test tube until the formation of the suspension began and the subsequent solution became turbid. The resulting suspension was again introduced onto the OSBPM disk and passed through the disk slowly to penetrate inside the C_{18} completely. The filtration and addition of water step was repeated until the passed solution became completely clear and BDSC spread on the whole disk surface. The disk was then washed with 10 mL of diluted nitric acid (0.01 M) and 25 mL of water and dried by passing air through it, repeatedly.

Copper recovery and measurement

The modified disk was washed with 25 mL of water to pre-wet the surface of the disk before the extraction. Then, 250 mL of the completely homogenized and non-miscellaneous aqueous solution containing 10 μg of Cu^{2+} which was buffered at pH=4, passed through the membrane disk (flow-rate = 30 mL min^{-1}). After the extraction, the disk was dried completely by passing air through it and a 23 mm × 200 mm test tube was placed under the extraction funnel. The adsorbed copper was then stripped from the membrane disk using different types of washing agents which were compatible with flame and didn't change the signal to noise ratio, at a flow-rate of 10 mL min^{-1} by proper eluents in the reverse direction. Then, the stripped copper was transferred into a 10 mL graduated volumetric flask. To ensure non-adsorption of trace copper on the inner layer of the test tube, it was washed with 2 mL of the eluent. Finally, the flask was diluted to the mark with the eluent and the copper concentration in eluate was determined at λ=324.7 nm by an external calibration curve.

RESULTS AND DISCUSSION

Elution of the trapped Cu^{2+} ions

According to the similar well documented reports [2-7] the results of extraction of trace copper are tabulated in Table 1.

Table1.Percentage recovery of Cu^{2+} through the modified OSBPM disk using different eluents [a]

Removal solution	**Recovery (%)**	
	5 mL	**10 mL**
HCl(3M)*	28.1 (2.1) [d]	51.3 (3.0)
HNO_3(1M)*	48.2 (6.4)	78.9(3.2)
HNO_3(3M)*	76.4(0.3)	99.4(0.9)
EDTA(1M)*	46.8(4.5)	100.6 (4.3)
CH_3OH	75.6(3.3)	99.9 (2.2)
Acidified CH_3OH [b]	54.4(2.4)	74.7(3.6)
Alkaline CH_3OH [c]	31.3(3.5)	43.1 (3.3)
C_2H_5OH	74.5(2.6)	98.9(1.1)
Acidized C_2H_5OH	31.8(1.7)	83.1(2.5)
Alkaline C_2H_5OH	22.6(0.9)	38.9(2.4)

[a] Initial samples contained 10 µg of Cu^{2+} in 250 mL of aqueous sample.
[b] Acidified organic solutions with HCl 0.1 M.
[c] Alkaline organic solutions obtained by using NH_3 0.1 M.
* Solutions containing methanol (2.5 % V V^{-1}).
[d] Values in parentheses are RSDs based on five replicate measurements

As can be seen from Table 1, the extraction is quantitative and satisfactory when 10 mL of methanolized HNO_3(3M), EDTA(1M) as well as CH_3OH and/or C_2H_5OH are employed. However, in all optimized experiments 10 mL of methanolized HNO_3(3M) was selected as the best stripping agent.

The effects of pH, modifier and flow-rates

The extraction was conducted over the pH range of 1-8 and modifier amount between 1 and 15 mg (Fig. 1 and Fig. 2). It was concluded that in the pH range 4-7 and BDSC amount ≥6 mg of BDSC, subsequent extraction was complete and reproducible. Furthermore, the optimized flow-rates concerning sample and eluents were found to be 30 and 10 mL min^{-1}, respectively.

Analytical performance

According to the proposed procedure, the maximum capacity of each OSBPM disk was determined by passing 250 mL portions of an aqueous solution containing 3000 µg of copper at pH 4.0 followed by the determination of the stripped Cu^{2+}contents using FAAS. The maximal capacity of the employed OSBPM disk with respect to copper was found to be 403±1.3 µg. The limit of detection (LOD) of the proposed procedures was 0.013 ng L^{-1}.

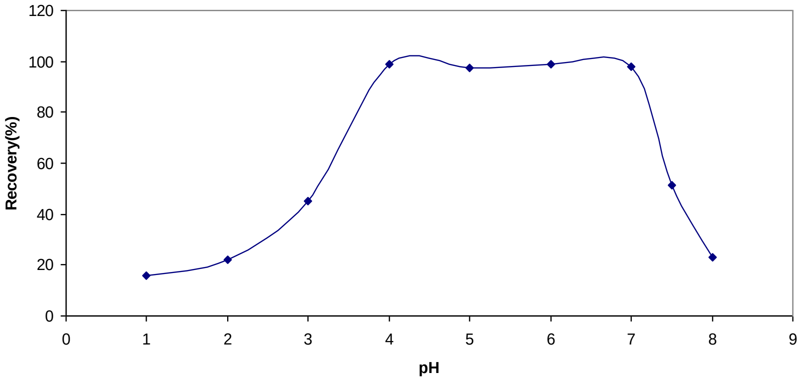

Figure 1. Effect of pH on the percent recovery of 10 μg of Cu^{2+} from 250 mL aqueous solution by each C_{18} disk impregnated with 6.0 mg of BDSC.

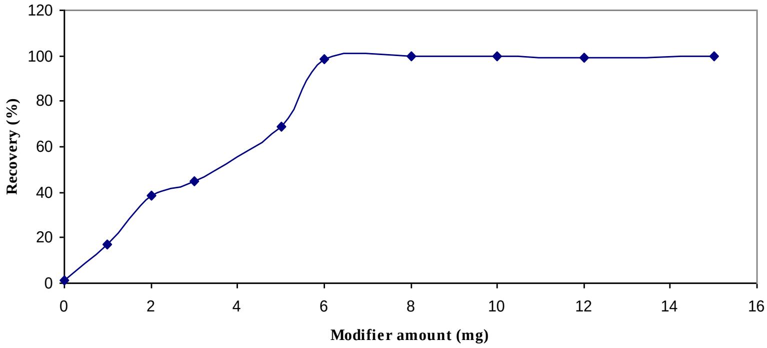

Figure 2. Percent recovery of 10 μg of Cu^{2+} from an aqueous solution (250 mL) by the membrane disk at a flow-rate = 30 mL min^{-1} at pH=4 washed by 10 mL of HNO_3 3.0 M at a flow-rate = 10 mL min^{-1} and varying amounts of BDSC.

Quantification of copper in real samples

To assess the applicability of the described method, it was utilized for selective extraction and determination of copper in different water samples (Table 2). As seen, the recovered copper ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICP-AES.

Table 2. Percent recovery of copper addition to 1000 ml of different real water samples

Sample	**Cu^{2+} added (μg)**	**Determined amount (μg L^{-1})**	
		Proposed method	**ICP-AES**
Tap water 1	0.0	20.1 (4.1) [b]	ND
	10.0	29.8 (3.4)	ND
Tap water 2	0.0	17.8 (2.1)	ND
	10.0	28.7(1.2)	ND
Well water	0.0	28.2(2.4)	ND
	10.0	39.5(5.5)	ND
Rain water	0.0	18.9 (0.7)	ND
	10.0	28.6(4.6)	ND
Snow water	0.0	20.1(0.9)	ND
	10.0	30.4(2.7)	ND
Spring water	0.0	10.2(1.5)	ND
	10.0	19.6(2.4)	ND
River water	0.0	9.8 (1.3)	ND
	10.0	20.1(6.3)	ND
Waste water 1	-	169.1(5.1)	169
Waste water 2	-	138.2(2.5)	139

[a] Not detected.

[b] Values in parentheses are RSDs based on five replicate analyses.

CONCLUSION

The results obtained from this attempt highlight the high potential of the proposed method for assessment of trace copper contents in diverse aqueous sample by using circular and flat octadecyl silica bonded phase membrane disks modified by BDSC and FAAS measurement. The method possesses a breakthrough volume of 2000, a concentration factor of 200 and detection limit of 0.013 ng L $^{-1}$. It also permits the rapid and straightforward determination of copper even in the presence of high amounts of diverse foreign ions involved in much real samples.

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