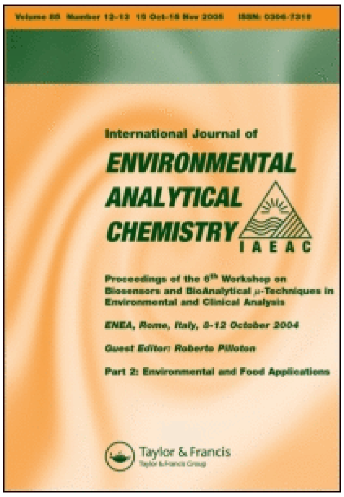

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PRECONCENTRATION OF TRACE AMOUNTS OF COPPER IN AQUEOUS SAMPLES BY OCTADECYL SILICA MEMBRANE MODIFIED DISKS AND DETERMINATION BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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A simple and reliable method for the rapid and selective separation of Cu(II) ion from water, waste water and black tea by using octadecyl silica membrane disks modified with an H_2Salphen (L) and flame atomic absorption spectrometry is presented. Extraction efficiency and the influence of flow rate, pH and minimum amount of stripping acid were investigated. Maximum capacity of the membrane disks modified by 2 mg of (L) was found to be 487.5 ± 7.5 µg of copper. The limit of detection of proposed method is 0.07 ng/cm^3.

Keywords: Copper (II); Solid phase extraction; Salphen; Flame atomic absorption spectrometry; Waste water; Black tea

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INTRODUCTION

The determination of copper in water samples is warranted by the narrow window of concentration between essentiality and toxicity [1,2]. Speciation analysis of water samples has focused on known toxic forms such as ionic copper [3]. Thus, the determination of trace amounts of copper becoming increasingly important because of the increased interest in environmental pollution. The most common methods for determination of copper ion are spectrophotometry [4–6], differential pulse anoding stripping voltammetry [7], flame and graphite furnace atomic absorption spectrometry [8], constant current stripping analysis [9], and potentiometry [10], but their sensitivity is usually insufficient for the low concentrations in environmental samples. Consequently, a preconcentration and matrix elimination step is usually required. The most widely used techniques for the separation and preconcentration of trace amounts of copper are liquid–liquid extraction (LLE) [11,12], absorption of copper complexes on the microcrystalline naphthalene [13] and preconcentration on C60–C70 fullerenes [14], activated carbon [15] as well as solid phase extraction (SPE) [16–17].

Solid phase extraction (SPE) is an alternative technique that reduces solvent usage and exposure, disposal cost, and extraction time for sample preparation [18]. Recently, hydrophobic SPE disks have been used extensively for the determination of organic environmental pollutants [19–20]. These disks, made of 90% (w/w) octadecyl silane in an inert polytetrafluoroethylene matrix, have atypical diameter of 47 mm and a thickness of 0.5 mm. Typical capacity of a disk for well-retained compounds ranges from 10 to 20 mg. The proclaimed major advantages of the SPE disks include (1) shorter sample processing time due to the large cross-sectional area of the disk and decreased pressure drop, which allows the sample processing at higher flow rates, (2) decreased plugging by particles due to large cross-sectional area of the disk and (3) reduced channeling resulting from the use of smaller diameter sorbent and a greater mechanical stability of the sorbent bed [21].

In recent years we have employed octadecyl silica membrane disks modified with different noncyclic and macrocyclic ligands to develop simple, fast and reliable methods for the selective separation, concentration and determination of Ba^{2+} [22], Pb^{2+} [23,24] UO_2^{2+} [25] from aqueous solutions. The aim of this work was the development of a simple, sensitive and concentration of trace amount of Cu^{2+} from aqueous media using octadecyl silica membrane disks modified with H_2Salphen and its determination by flame atomic absorption spectrometry (FAAS).

EXPERIMENTAL

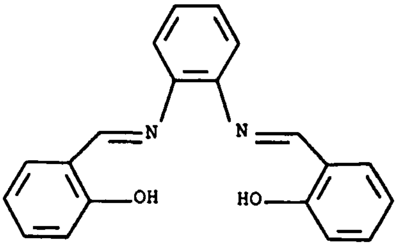
Reagents

Hydrobromic acid, hydrochloric acid, acetic acid and nitric acid, high purity methanol, (all from Merck) were used as received. Analytical grade copper nitrate and other salts (all from Merck) were of the highest purity available and were dried in a vacuum over P_2O_5.

Synthesis of the H_2Salphen

The H_2Salphen (L) was prepared by a previously reported method [26] as follows: 1,2-phenylenediamine, 0.54 g (5.0 mmol), was dissolved in 30 cm^3 of ethanol and then transferred into a 250 cm^3 three-necked flask. Under reflux 1.22 g (10.0 mmol) of salicylaldehyde in 25 cm^3 of ethanol was added drop wise to the flask. The stirred mixture was kept reacting for 60 min, under reflux, and then cooled to room temperature. The solid product was filtered, and the product was recrystallized from ethanol and vacuum-dried for 12 h. ^{1}H-NMR: δ 6.8–7.6 (m, 12H, phenyl), 8.8 (s, 2H, -CH = N-), 13 (s, 2H, OH).

IR (ν, cm^{-1}) 1620 s, 1590 s, 1550 s, 1475 s, 1450 s, 1290 s, 1210 m, 1150 m, 1120 w, 1020 m, 930 m, 830 m, 750 s, and a very broad bond at 3000 cm^{-1}.



(L)

Apparatus

The copper determination was carried out on a Perkin–Elmer 603 atomic absorption spectrometer with a hollow cathode lamp and a deuterium background corrector. The AAS determination of all other cations was performed under the recommended conditions for each metal ion.

Extraction was performed with 47 x 0.5 mm (diameter x thickness) Empore membrane disks containing octadecyl-bonded silica (8-μm particles 60-Å pore size, 3M Co., Paul, MN). The disk was used in conjunction with a standard Millipore 47-mm filtration apparatus.

Preparation of the SPE membrane disks

To remove potential interferences and to ensure optimal extraction of the analyte of interest, the disk cleaning and conditioning should be done before its use. Thus, after placing the membrane disk in the filtration apparatus, 10 cm^3 of methanol was poured onto the disk immediately and drawn through the disk by applying a slight vacuum. After all of the solvent has passed through the disk, air was passed through it for few minutes. The disk conditioning was then performed by pouring 10 cm^3 of methanol onto the disk. Immediately, a low vacuum was applied and the solvent was drawn through the disk until the solvent surface almost reached the surface of the disk. The disk should not be allowed to soak without vacuum, and air should not be allowed to make contact with the disk surface. Immediately, 10 cm^3 of water was introduced onto the disk and was drawn through the disk. The disk was then dried under vacuum for 5 min, this is especially important for the disks that are used for the first time. Finally, a solution of 2 mg of (L) dissolved in 1 cm^3 of methanol was introduced onto the disk so that the solution was spread on the whole disk surface. The solution was allowed to penetrate inside the membrane completely without applying any vacuum. After about 1 min, the filtration funnel containing the modified disk was transferred into an oven and the solvent was completely evaporated at 60°C. Then the sample solution containing Cu^{2+} was passed through the membrane. After the extraction, copper ion was stripped from the membrane disk using appropriate amounts of a hydrochloric acid solution. Then the copper concentration was determined by flame atomic absorption spectrometry.

RESULTS AND DISCUSSION

In preliminary experiments, the complexation of H_2Salphen (L) with a number of transition and heavy metal ions was investigated conductometrically in acetonitrile solution at $25 \pm 0.1°C$ [27,28], in order to obtain a clue about stability and selectivity of the resulting complexes. The formation

TABLE I Percent recovery of copper from the modified membrane disks using different stripping acid solutions[a]

Stripping acid solution	*% Recovery (Volume* (cm^3))			
	5	*7.5*	*15*	*20*
HNO_3 (3 M)	41	64	77	100
HBr (3 M)	49	70	88	100
CH_3COOH (3 M)	14	23	41	100
HCl (3 M)	92	100	100	100
HCl (2 M)	70	88	97	100
HCl (1 M)	60	72	88	100
HCl (0.5 M)	34	53	69	74

[a] Initial samples contained 20 μg Cu^{2+} ion in 50 cm^3 water.

constants K_f of the resulting 1 : 1 complexes were determined by computer fitting of the molar conductance–mole ratio data to an appropriate equation [27,28]. The stability of the resulting complexes varied in the order $Cu^{2+} \gg Zn^{2+} > Hg^{2+} > Pb^{2+} > Ni^{2+} > Cd^{2+} > UO_2^{2+} > Co^{2+}$. Thus, the ligand (*L*) is expected to act as a suitable modifier for selective solid phase extraction of Cu^{2+} ions.

Some primary experiments were carried out in order to choose a proper eluent for the retained Cu^{2+} ions after the extraction of 20 μg copper in 50 cm^3 solution by the modified disks. The retained copper ions were then stripped with varying volumes of different acid solutions of varying concentration (Table I). From the data given in Table I, it is immediately obvious that among five different acid solutions used, 7.5 cm^3 of 3.0 M hydrochloric acid can accomplish the quantitative elution of copper from the membrane disk, while other acids used are ineffective for the complete elution of copper.

The influence of flow rates of the sample and stripping solutions from the modified membrane disk on the retention and recovery of copper(II) ion was investigated. It was found that, in the range of 1–30 cm^3 min^{-1}, the retention of copper by the membrane disk is not affected by the sample solution flow rate considerably. Similar results for the extraction of organic and inorganic materials [19,20,22–25] by octadecyl silica disks have already been reported in the literature. On the other hand, quantitative recovery of Cu^{2+} ions from the modified membrane disks was achieved in a flow rate range of 1.0–10 cm^3, using 7.5 cm^3 of 3.0 M hydrochloric acid as a stripping solution. However at higher flow rates, larger volumes of 3.0 M hydrochloric acid were necessary for quantitative stripping of Cu^{2+} ions.

In order to investigate the optimum amount of (L) on the quantitative extraction of copper by membrane disk, copper ion extraction was conducted by varying the amount of ligand from 0 to 10 mg and results are summarized in Table II. As seen, the extraction of copper is quantitative using above 2 mg of (L). Hence, subsequent extraction experiments were carried out with 2 mg of (L).

The influence of the pH of aqueous samples on the recovery of 20 μg Cu^{2+} from 50 cm^3 solutions was studied in a pH range of 2.0–8.0. The pH was adjusted by using 0.1 M of either nitric acid or sodium hydroxide solutions. The results are shown in Fig. 1. As can be seen from Fig. 1 at pH range

TABLE II Effect of amount of (*L*) on Cu^{2+} ion extraction[a]

Amount of L (mg)	*% Recovery*
0	0
1	56.0 (1.5)[b]
2	100.0 (1.3)[b]
3	99.9 (1.7)[b]
4	99.8 (1.3)[b]
5	99.7 (1.8)[b]
10	99.8 (1.5)[b]

[a] Initial samples contained 20 μg Cu^{2+} ion in 50 cm^3 water.

[b] Values in parentheses are RSDs based on three replicate analysis.

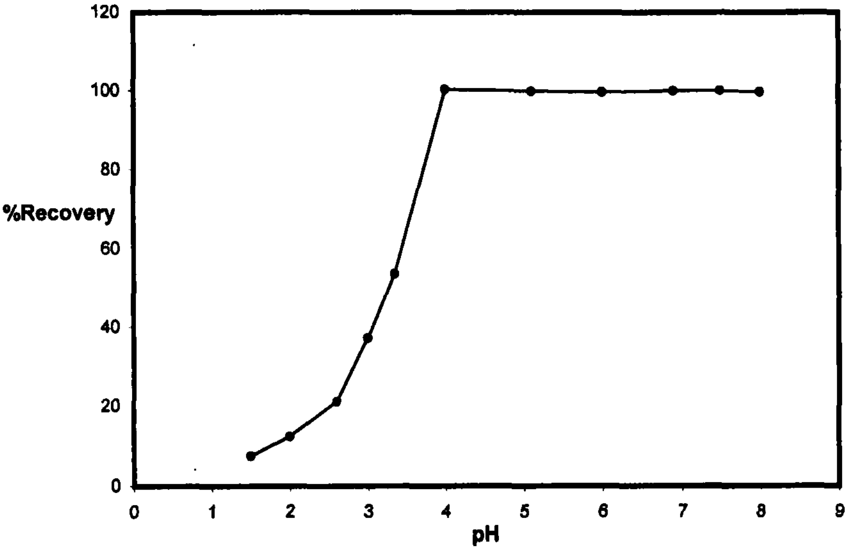


FIGURE 1 Effect of pH on recovery of copper(II)

4.0–8.0 the modified membrane disk can retain the Cu^{2+} ions quantitatively. The observed reduce on recovery of copper at lower pH values could be due to protonation of the (L). Higher pH values (>8.0) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks.

The break-through volume of sample solution was tested by dissolving 20 μg of copper in 25, 50, 100, 250, 500, 1000, 1500 and 2000 cm^3 water and the recommended procedure was followed. In all cases, the extraction by modified membrane disk was found to be quantitative. Thus the break-through volume for the method should be greater than 2000 cm^3.

The limit of detection (LOD) of the proposed method for the determination of copper was studied under the optimal experimental conditions. The LOD obtained from $C_{LOD} = K_b S_b m^{-1}$ [29,30] for a numerical factor $K_b = 3$, is 0.07 ng per cm^3.

The maximum capacity of the membrane disk modified by 2 mg of (L) was determined by passing 25 cm^3 portions of an aqueous solution containing 2000 μg copper through the disk, followed by determination of the retained metal ions using FAAS. The maximum capacity was found to be 487.5 ± 7.5 μg of Cu^{2+} ions on the disk.

In order to investigate the selective separation and determination of Cu^{2+} ion from its binary mixtures with diverse metal ions, 25 cm^3 of aqueous solutions containing 20 μg Cu^{2+} and various amounts of other cations were taken and the recommended procedure was followed. The results are summarized in Table III. The results show that the copper ions in the binary mixtures are retained almost completely by the modified membrane disk. Meanwhile, retention of other cations by the disk is very low and they can be separated from Cu^{2+} ion.

TABLE III Separation of copper from binary mixtures[a]

Diverse ion	*Amount taken* (mg)	*% Found*	*% Recovery*
Na^+	10	NADP[b]	99.9 (1.2)[c]
K^+	15	NADP	98.9 (1.1)
Mg^{2+}	10	NADP	100.1 (1.4)
Ca^{2+}	14	NADP	99.8 (1.5)
Sr^{2+}	16	NADP	99.1 (1.6)
Co^{2+}	10	0.5 (0.2)	99.7 (1.4)
Cd^{2+}	15	0.5 (0.1)	99.7 (1.2)
Ni^{2+}	8	0.1 (0.1)	99.8 (1.5)
Pb^{2+}	14	0.8 (0.3)	100.3 (1.4)
Zn^{2+}	12	0.9 (0.4)	99.1 (1.1)

[a] Initial samples contained 20 μg Cu^{2+} ion in 100 cm^3 water.
[b] No adsorption, passes through disk.
[c] Values in parentheses are RSDs based on three replicate analyses.

In order to assess the applicability of the method to real samples, with different matrices containing varying amounts of a variety of diverse ions, it was applied to the separation and recovery of copper ions from three synthetic samples as well as two different wastewater and black tea samples. Table IV shows the recovery of 20 μg of added copper ion from 100 cm^3 of different synthetic water samples. As can be seen, the results of three analyses of each sample show that the copper recovery was almost quantitative. Table V shows the concentration of copper ion in two different wastewater samples (Tehran copper electroplating factory, Tehran, Iran). As seen, the results of three analyses of each sample obtained by the proposed method and ICP-AES are in satisfactory agreement. The proposed method was also applied to the determination of copper ion in two black tea samples. The procedure used for the extraction of copper from tea sample was similar to that the reported in the literature. One gram of the dry tea sample (dried at 110°C) was placed in a 50-cm^3 beaker, followed by the addition of 7 cm^3 of concentrated nitric acid, and the beaker was covered with a glass watch. The beaker was allowed to stand over night, and the contents were heated on a hot plate (150°C for 15 min). Then the sample was cooled, 8 cm^3 of perchloric acid was added, and the mixture was heated again at 200°C until the solution became clear (about 1 h). The glass watch was removed and the acid evaporated to dryness at 150°C.

TABLE IV Recovery of 20 μg copper added to 25 cm^3 solution of the synthetic and water samples

Sample	*% Recovery of Cu^{2+} ions*
Synthetic sample 1 (Pb^{2+}, Cd^{2+}, Zn^{2+} and Ni^{2+}, 2 mg of each cation)	98.9 (1.5)[a]
Synthetic sample 2 (Na^+, K^+, Mg^{2+} and Ca^{2+}, 3 mg of each cation)	99.7 (1.1)[a]

[a] Values in parentheses are RSDs based on three replicate analysis.

TABLE V Determination of copper in wastewater samples

Sample	*Cu* (μg/cm^3) *(SPE)*	*Cu* (μg/cm^3) *(ICP)*
1	0.11 (0.01)[a]	0.12 (0.2)
2	0.13 (0.01)	0.13 (0.02)

[a] Values in parentheses are RSDs based on three replicate analyses.

TABLE VI Determination of copper in black tea samples

Sample	*Cu* (µg/cm^3) *(SPE-AA)*	*Cu* (µg/cm^3) *(ICP)*
Iranian black tea (Lahijan)	56.4 (0.3)[a]	56.1 (0.2)
Indian black tea (Seylon)	39.7 (0.3)	39.9 (0.2)

[a] Values in parentheses are RSDs based on three replicate analyses.

The white residue was completely dissolved in 5 cm^3 of 1 M nitric acid and the solution was transferred to a 100-cm^3 calibrated flask. Then, the solution was neutralized with a proper LiOH solution. Finally, 10 cm^3 of a 0.1 M lithium acetate/acetic acid buffer solution of pH 5.5 was added and the solution was diluted to the mark [31], and the recommended procedure was followed. The results are shown in Table VI. As can be seen, the amount of copper in black tea can be accurately determined with the proposed method.

CONCLUSION

In this work, trace amounts of Cu(II) ions in aqueous solutions were selectively separated and preconcentrated on octadecyl silica membrane disks modified with a H_2Salphen as a novel copper complexing agent. Flame atomic absorption spectrometry was used for the determination of copper ions. The proposed method has the following advantages. The method is rapid, the time taken for the separation and analysis of copper in a 100 cm^3 water sample is at the most 20 min. It can selectively separate Cu^{2+} ion from other metal ions associated, even at much higher concentrations. The method can be successfully applied to separation and determination of copper in water, wastewater and black tea.

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