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Preconcentration and spectrophotometric determination of copper(II) using octadecyl silica membrane disks modified by 1-nitroso-2-naphthol-3,6-disulfonic acid

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ABSTRACT

A simple and fast method for extraction and determination of trace amounts of copper(II) ions using octadecyl-bonded silica membrane disks modified with 1-nitroso-2-naphthol-3,6-disulfonic acid and visible spectrophotometry at a wavelength maximum of 636 nm is introduced. Extraction efficiency and the influence of flow rates, pH, and type and smallest amount of stripping acid were investigated. Maximum capacity of the membrane disks modified with 2 mg of the anthraquinone derivative used was found to be 489µg Cu^{2+}. The limit of detection of the proposed method is 10 ng/ml. The method is applied to the recovery of Cu^{2+} from different synthetic samples and a spring water sample.

Key words*:* Copper(II) ;SPE; Octadecyl slica disks; Visible spectrophotometry; 1-nitroso-2-naphthol-3,6-disulfonic acid.

INTRODUCTION

Copper is both vital and toxic for many biological systems[1,2] . Thus, the determination of trace amounts of Cu is becoming increasingly important because of the increased interest in environmental pollution[3]. Flame and graphite furnace atomic absorption spectrometry and spectrophotometric methods provides accurate and rapid determination of copper in natural waters and wastewaters [4] . Nevertheless, very frequently for the extremely low concentration copper in waters, a direct determination cannot be applied without their previous preconcentration and separation.The most widely used techniques for the separation and preconcentration of trace amounts of Cu are liquid_liquid extraction 4 , precipitation[5,6] and chelating resins[7] . The large distribution ratios possible in solvent extraction systems allow the analytical determination of substances present in otherwise non detectable concentrations.

A proper choice of extractant may lead to an increase in concentration by several orders of magnitude. In other words, a large increase in sensitivity is obtained in the analytical method, even when the analyte is analytically detectable in the original sample, its preconcentration by means of solvent extraction permits use of smaller samples, simplification of the procedure, and increased accuracy of the samples. Very often, both separation and preconcentration are required, and an advantage of solvent extraction is that both can be obtained in the same step [8]. Solvent extraction of metal chelate complexes has been used as a separation method for a long time. Recovery of metals from an aqueous phase by solvent extraction is achieved by contacting the aqueous phase with an organic phase that contains a metal selective chelating agent dissolved in a diluent [9] . For extraction of metal ions, it is preferable that the chelating reagent used has a high distribution coefficient and pH dependence in the system chosen [10-14].Different methods, especially Liquid. Liquid extraction of copper in the presence of various classical [15-19] and macrocylic [20, 21] co extractant ligands has attracted considerable attention. However, the use of classical extraction methods for this purpose is usually time consuming, labor intensive and requires large amounts of high purity solvents for extraction. Nevertheless, several other techniques for the preconcentration and separation of copper have been proposed including liquid chromatography[22] supercritical fluid extraction[23], flotation[24], aggregate film formation[25], liquid membrane[26], column adsorption of pyrocatechol violet copper complexes on activated carbon[27], ion pairing [28], ion pairing[29], preconcentration with yeast[30], and solid phase extraction using C_{18} cartridges and disks[31-33].

Solid phase extraction (SPE) or liquid solid extraction is poplar and growing techniques that are used to sample preparation for analysis. It is an attractive alternative for classical liquid liquid extraction methods that reduce solvent usage and exposure, disposal costs and extraction time for sample separation and concentration purposed [34-36]. In recent years, the octadecyl bonded silica SPE disks have been utilized for the extraction and separation of different organic compounds from environmental matrices[37-40]. Moreover, the SPE disks modified by suitable ligands are successfully used for selective extraction and concentration of metal ions [41-42,46].

In a recent series of papers, [43-45] we have described the application of metal. DNA conjugates to nucleic acid sequence determination with catalytic signal amplification, the assay relies on the esterase activity of a DNA. linked Cu complex. For optimization of the system and exploration of structure activity relationships, a sensitive probe would be useful, which allows straightforward detection of esterase activity of ligated Cu^{2+} in low concentration.The aim of this work was the development of a rapid, efficient and highly sensitive method for selective extraction and concentration of ultra trace amounts of Cu^{2+} ions from aqueous media using octadecyl silica membrane disks modified by 1- nitroso, 2-naphthol, 3,6 disulfonic acid **I** and visible spectrophotometry determination.

MATERIAL AND METHODS

Reagents

All acids were of the highest purity available from Merck Chemical Company and were used as received. Acetonitrile, methanol, and 2. propanol were of HPLC grade from Aldrich Chemical Company. Analytical. grade nitrate salts of copper, sodium, magnesium, calcium, strontium, barium, cobalt, nickel, lead, zinc, cadmium, and mercury (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Double. distilled, deionized water was used throughout.

1-Nitroso, 2-naphthol. 3,6-disulfonic acid were obtained from Aldrich and High Purity double distilled deionized water was used throughout the experiments.

Apparatus

Determination of Cu^{2+} contents in working samples were carried out by a Jasco V. 576 (Japan) model double beam UV–Vis spectrophotometer fitted with tungsten lamp as the source was used for absorbance measurements. The 1 cm matched quartz cells were used for measuring the absorbance. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

Sample extraction

Solid phase extractions were carried out by glassy membrane disks, ENVI. 18DISK™ 47mm diameter ×0.6 mm thickness containing octadecyl silica bonded phase (30 µm particles, 70 A° pore size) obtained from Supelco in conjunction with a standard Millipore 47 mm filtration apparatus equipped with a vacuum pump.

After the membrane was placed in the filtration apparatus, it was washed with 10 ml methanol and then with 10 ml acetonitrile to remove all contaminants arising from the manufacturing process and the environment. After the disk was dried by passing air through it for several minutes, a solution of 2 mg **I** dissolved in 2 ml of 2. propanol was introduced into the reservoir of the apparatus and drawn slowly through the disk by applying a slight vacuum until the ligand penetrated the membrane completely. The solvent was evaporated at 50°C. Finally, the disk was washed with 25 ml water and dried by passing air through it. The membrane disk modified with **I** was now ready for sample extraction.

The general procedure for the extraction of Cu^{2+} ions on the modified membrane disk was as follows. The disk was first washed with 25 ml water. This step prewets the surface of the modified disk prior to the extraction of Cu^{2+} from water. Then 500 ml of the sample solution containing 10 µg Cu^{2+} was passed through the membrane (flow rate = 20 ml min^{-1}). After extraction, the disk was dried completely by passing air through it for a few minutes. The extracted copper was then stripped from the membrane disk using 20 ml of a 1 M solution of nitric acid into a 25.0 ml volumetric flask and diluted to the mark with water, and the copper concentration was determined by visible spectrophotometry.

RESULTS AND DISCUSSION

It is well known that various derivatives of carbodithioates are able to form stable 2:1 (ligand:metal) complexes with a variety of metal ions in some nonaqueous solvents[51, 52], the resulting Cu^{2+} complexes are among the most stable complexes formed[55.] Due to its water insolubility as well as its tendency to form a selective and stable complex with Cu^{2+} [55], the synthetic **I** was employed in this work as a proper ligand for selective SPE of copper from aqueous solutions. Thus, some preliminary experiments were carried out to investigate the quantitative retention of Cu^{2+} by the octadecyl silica membrane disks in the absence and presence of **I.** It was found that, while the membrane disk itself does not show any tendency for the extraction of copper ions, a membrane disk modified with **I** is capable of retaining Cu^{2+} in the sample solutions quantitatively (the test solutions used contained 0.1 and 1.0 µg copper in 10 ml water). This is most probably due to the existence of a strong interaction between Cu^{2+} and the carbodithioate used.

To choose a proper eluent for the retained Cu^{2+} on the modified disks, after extraction of 10 µg copper from 500 ml water, the copper ions were stripped with varying amounts of 1 M concentrations of different acids and the results are summarized in Table 1. It is seen that the elution of copper from the modified membrane disk was quantitative with 20 ml of 1M HNO_3, while this could not be done even with greater than 25. ml volumes of the other acids tested. In other experiments it was found that the lower the concentration of nitric acid, the larger the volume of acid solution needed for the quantitative stripping of the cations. Thus, 20ml portions of 1 M HNO_3 were used for further studies. It is noteworthy that when nitric acid of concentrations higher than 1 M was used, there was some leaching of **I** from the disk.

The influence of flow rates of the sample and stripping solutions from the modified membrane disks on the retention and recovery of 10 µg of copper ions was investigated. It was found that, in the range 1–60 ml min^{-1}, the retention of copper by the membrane disk is not affected by the sample solution flow rate considerably. Some similar results for the extraction of organic[47,49] and inorganic materials[50,51] by octadecyl silica disks have already been reported in the literature. On the other hand, quantitative stripping of Cu^{2+} ions from the modified membrane disks was achieved in the flow rate range 0.5–5 ml min^{-1}, using 20 ml of 1 M HNO_3 as stripping solution. At higher flow rates, larger volumes of 1 M HNO_3 were necessary for quantitative stripping of Cu^{2+}.

The effect of the pH

The pH of the sample solutions were adjusted to different values between 2.9 by addition of hydrochloric acid or a suitable buffer such as sodium acceate. acetic acid or sodium dihydrogen phosphate disodium hydrogen phosphate, and then solutions passed through the disks.

Eventually, the metal ions were stripped by pure methanol or ethanol solutions followed by visible spectrophotometry determination of the eluted copper(II).Then, percentage recovery at various pH values was determined(Fig .1). According to the results shown in Fig.1 up to pH 5.0. 5.5, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is due to fact that in an acidic solution the protonation of **I** occurs and there is a weak tendency for retention between Cu(II) and **I**, whereas at higher values (pH>5), Cu(II) reacts with hydroxide ions to produce $Cu(OH)_2$. Therefore, sodium acceate. acetic acid buffer with pH=5 was used for the preconcentration step. Other solvents used for dissolving **I** were methanol and ethanol. The influences of these solvents on the recoveries as a function of pH are compared and shown in

Table 1: Percentage recovery of copper ion from the modified membrane Disks using different volumes of 1 m solutions of different acids[a]

Acetic	Recovery (%)			Volume
	Hydrochloric acid	Hydrobromic acid	Nitric acid acid	(ml)
22.9	35.7	38.6	40.8	5
39.7	46.4	47.9	64.5	10
48.5	69.5	68.5	88.4	15
78.2	79.3	83.6	99.3	20
82.0	85.2	92.0	98.2	25

[a] Initial samples contained 10 µg Cu^{2+} in 1000 ml solution.

Table 2: Separation of Copper from Binary Mixtures [a]

Recovery of Cu^{2+}(%)	Diverse found ion (%)	Amount taken (mg)	Diverse ion
99.8 (1.9)[c]	NAPD[b]	2.1	Na^+
98.2 (1.7)	NAPD	2.2	Mg^{2+}
99.0 (1.8)	NAPD	2.2	Ca^{2+}
98.0 (1.9)	2.5 (1.1)	2.7	Sr^{2+}
99.8 (2.5)	NAPD	2.4	Ba^{2+}
99.7 (1.7)	NAPD	2.7	Co^{2+}
94.5 (1.7)	NAPD	1.9	Ni^{2+}
99.4 (1.6)	NAPD	1.3	Pb^{2+}
97.8 (1.5)	NAPD	2.7	Zn^{2+}
100.6 (2.8)	NAPD	1.8	Cd^{2+}
98.5 (1.9)	NAPD	1.8	Hg^{2+}

[a] Initial samples contained 10 µg Cu^{2+} and different amounts of diverse ions in 1000 ml water.

[b] No adsorption, passes through disk.

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

Table 3: Recovery of 10 µg Copper Added to 1000-ml Solutions of the Synthetic and Water Samples

Recovery of Cu^{2+} (%)	Sample
97.8 (2.3)	Synthetic sample 1 (Na^+,Mg^{2+},Ca^{2+},Co^{2+},Hg^{2+}, 2 mg of each cation)
97.9 (2.7)	Synthetic sample 2 (Na^+,Mg^{2+},Sr^{2+},Ba^{2+},Co^{2+}, Hg^{2+}, 2 mg of each cation)
98.5 (2.5)	Synthetic sample 3 (Na^+,Mg^{2+},Zn^{2+},Cd^{2+},Hg^{2+}, 2 mg of each cation)

Fig. 1. Mean while, other organic solvents were not tested because of their restricted solubility and formation of two phases with aqueous solutions and incompatibility with flame . Higher pH values (>7) were not tested because of the possibility of the hydrolysis of octadecyl silica.

Disk efficiency

Undoubtedly, one of the major parameters affecting in the SPE determinations is the efficiency of the used membrane disks. However, to the best of our knowledge this case has not been discussed elsewhere in similar reports. Under the optimum experimental conditions, it was found out that each ENV. 18 DISK^{TM} disk could perform at least 15 replicate analyses if organic eluting solvents are used. On the other hand, acidic, eluents practically decrease the number of time a disk could be used to 10replicates. These observations are represented in Fig. 2.

The maximum capacity of the membrane disk modified with 2 mg of **I** was studied by passing 500. ml portions of an aqueous solution containing 2000 µg copper through the disk, followed by determination of the retained metal ions using visible spectrophotometry. The maximum capacity of the disk thus obtained was found to be 489µg of Cu^{2+} on the disk.

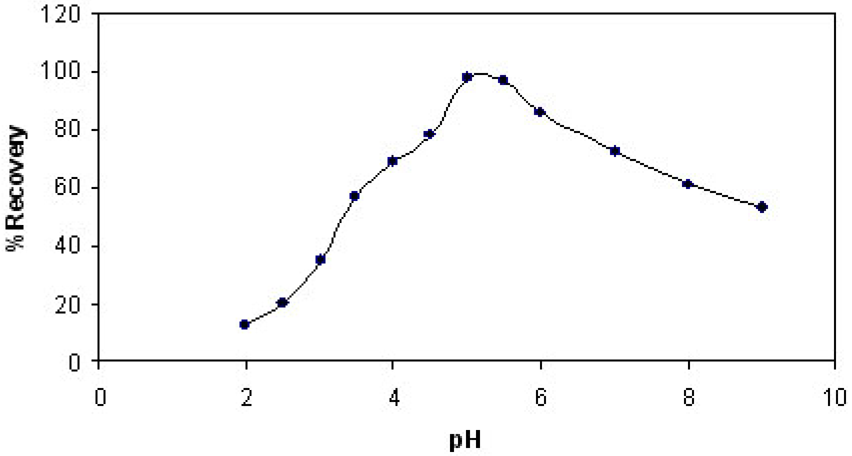

Fig. 1: Influence of sample pH and dissolving solvent of I on the percentage recovery of Cu(II)

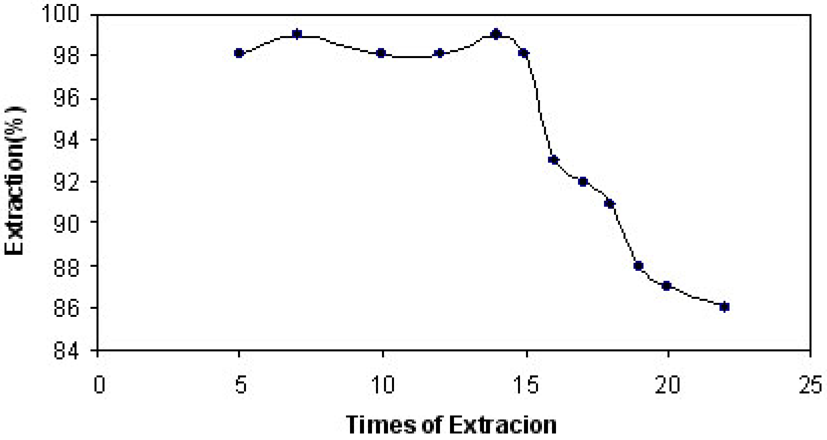

Fig. 2: Influence of eluent type on disk efficiency

Table 4: Recovery of copper added to 1000mL of different water samples (contaning 0.1M acetate at pH= 5.5-6.0)

Sample	Cu^{2+} added (µg)	Cu^{2+} determined (ng .mL^{-1})
Tap water	0.010.0	1.98(1.9)[a]12.22(1.3)
Snow water	0.010.0	4.89(1.9)14.89(1.9)
Rain water	0.010.0	2.49(1.7)12.70(1.9)
Sea Water	0.010.0	13.55(1.7)23.97(1.8)

The breakthrough volume of sample solutions was tested by dissolving 10 µg of copper in 50, 250, 500, 1000, and 1500 ml water and applying the recommended procedure. In all cases the extraction by the membrane disk was found to be quantitative. Thus, the breakthrough volume for the method should be greater than 1500 ml. The limit of detection (LOD) of the proposed method for the determination of copper(II) was studied under optimal experimental conditions. The LOD obtained from $C_{LOD}= K_b S_b$ m^{-1}[56, 57] is 10 ng ml^{-1}. The reproducibility of the proposed method for the extraction and determination of 10 µg Cu^{2+} from 500 ml water was also studied. The results obtained on 10 replicate measurements revealed a RSD of 2.0%.

To investigate the selective separation and determination of Cu^{2+} from its binary mixtures with diverse metal ions, an aliquot of an aqueous solution (1000 ml) containing 10 µg Cu^{2+} and milligram amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table 2. The data in Table 2 reveal that Cu^{2+} in binary mixtures is retained almost completely by the modified membrane disk, even in the presence of up to 2100 µg of the diverse metal ions. It is interesting to note that, with the exception of Sr^{2+}, retention of other cations by the modified disk is negligible and they can be separated completely for the Cu^{2+} ion. However, in the case of Sr^{2+}, its retention by the disk is only 2.5%, which seems to be relatively low. It should be mentioned that the accompanying anions were found to have no measurable effect on the retention and recovery of copper ions.

Analysis of water samples

The applicability of the method to real samples with different matrices containing different amounts of a variety of diverse ions was assessed by using it to separate and recover copper ions from different synthetic and water samples. The results are given in Table 3. The results of three analyses of each sample show that, in all cases, copper recovery is almost quantitative.

To assess the applicability of the method to real samples, it was applied to the extraction and determination of copper from different water samples. Tap water(Tehran, taken after 10 min operation of the tap),rain water(Tehran, 20 January, 2009), Snow water (Saveh , 12 February,2009)and Sea water(taken from Caspian sea, near the Mahmoud. Abad shore) samples were analyzed(Table 4). As can be seen from Table 4 the added copper ions can be quantitatively recovered from the water samples used.

CONCLUSION

The proposed method is simple, highly selective, and reproducible. The reproducibility of the procedure is at the most 2%. It is rapid compared with the previously reported procedures for the separation and determination of copper[51-55], the time taken for the separation and analysis of copper ion in a 1000 ml water sample is at most 20 min. The method can be successfully applied to the separation and determination of copper in real samples.

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