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# Solid Phase Extraction and Pre-concentration of Sub-PPB Level of Copper in Aqueous Samples on Octadecyl Silica Membrane Disks Modified with a New Anthraquinone Derivative and Its Determination by Atomic Absorption Spectrometry

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# Solid Phase Extraction and Pre-concentration of Sub-PPB Level of Copper in Aqueous Samples on Octadecyl Silica Membrane Disks Modified with a New Anthraquinone Derivative and Its Determination by Atomic Absorption Spectrometry

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## ABSTRACT

A simple and reliable method for rapid and selective separation and preconcentration of trace amounts of $Cu^{2+}$ ions from different aqueous samples for the measurement by atomic absorption spectrometry is presented. By the passage of aqueous samples through an octadecyl-bonded

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silica membrane disk modified by 1-hydroxy-2-(prop-2′-enyl)-4-(prop-2′-enyoxyl)-9,10-anthraquinone, the $Cu^{2+}$ ions adsorb quantitatively and almost all matrix elements will pass through the disk to drain. The retained copper ions are then stripped from the disk by a minimal amount of nitric acid as eluent. The proposed method permitted large enrichment factors of 400 and higher. The limit of detection of the method is 100 ng $Cu^{2+}$ per 1000 mL. The effects of various cationic interferences on the recovery of copper in binary mixtures were studied. The method was successfully applied to the determination of copper in SRM bovine liver, tea leaves, and a synthetic seawater sample.

*Key Words:* Copper(II); SPE; Octadecyl silica disks; Anthraquinone; FAAS.

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## INTRODUCTION

Since copper is both vital and toxic for many biological systems,[1,2] its determination in aqueous samples is warranted by the narrow window of concentration between essentiality and toxicity.[3] Moreover, as an important element in geochemistry, copper can be easily released from sulfites, oxides, and silicates after some physical and chemical weathering, and after transport by water, it can accumulate in soils and sediments.[4] Thus, the trace amount analysis of copper from different matrices is an increasingly important task. Although flame and graphite furnace atomic absorption spectrometry[5] and spectrophotometric methods[6,7] are among the most widely methods used for copper determination, their sensitivity is usually insufficient for monitoring the low level concentrations of copper in environmental samples. Consequently, a preconcentration and matrix elimination process is usually required. In this respect, the liquid–liquid extraction of $Cu^{2+}$ ions with organic solutions containing different chelating agents[6,7] and macrocyclic ligands[8,9] has attracted considerable attention. However, these methods are usually labor-intensive, time-consuming, and require large volumes of high purity solvent.

In recent years, solid phase extraction (SPE) methods employing a variety of trapped ligands on different solid matrices have been successfully used for the preconcentration, separation, and sensitive determination of trace metal ions.[10–15] The use of SPE technique significantly reduces the consumption and exposure to solvent, disposal costs, and extraction time. Recently, there were several reports on the successful use of SPE disks for the extraction of several organic[16–18] and inorganic analytes.[11,19–23]

In recent years, we have been involved in the synthesis,[24] acid–base,[25,26] and electrochemical studies[27,28] and analytical applications of

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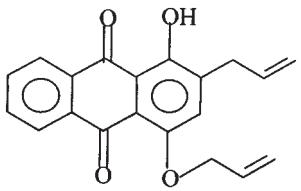
some new derivatives of 9,10-anthraquinone.[20,23,29–31] The aim of this work was the development of an efficient, reliable, and relatively rapid method for the selective extraction and concentration of ultra trace amounts of copper in aqueous media by octadecyl silica membrane disks modified with a recently synthesized anthraquinone derivative (1-hydroxy-2-(prop-2′-enyl)-4-(prop-2′-enyloxy)-9,10-anthraquinone, AQ) as a highly selective and stable reagent, and its determination with FAAS. It is worth mentioning that we have recently used AQ as an excellent ion-carrier in preparation of a highly selective PVC-based potentiometric sensor for $Cu^{2+}$ ion.[32]

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## EXPERIMENTAL

### Reagents and Samples

Extra pure methanol, nitric acid, hydrochloric acid, perchloric acid, acetic acid, and sulfuric acid (all from Merck) were used as received. The nitrate or chloride salts of the cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying. The anthraquinone AQ was synthesized, purified, and dried as it was described elsewhere.[24,33] Doubly distilled deionized water was used throughout. The standard stock solution of copper(II) (1000 ppm) was prepared by dissolving 1.0000 g of copper wire (99.99%) in the least amount of $HNO_3$ and dilution to 1000 mL in a calibrated volumetric flask with water. Working solutions were prepared by a appropriate dilution of the stock solution with water daily, 0.1-M acetate and phosphate buffer solutions were used for the pH ranges 4.0 to 5.5 and 6.0 to 7.5, respectively.

The synthetic seawater solution was prepared from high purity chloride salts of sodium, potassium, magnesium, and calcium and distilled water. The final solution contained 10,560 mg $L^{-1}$ sodium, 1270 mg $L^{-1}$ magnesium, 400 mg $L^{-1}$ calcium, 380 mg $L^{-1}$ potassium, and 10 μg $L^{-1}$ copper. This solution had the same matrix as a seawater sample. The pH of this solution was adjusted by hydrochloric acid and sodium hydroxide for preconcentration and matrix separation studies.

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The wet ashing of tea leaves and bovine liver was performed according to the following procedure. About 0.5 g of the dry sample (tea leaves dried at 110°C) was placed in 100-mL beakers, followed by the addition of 10 mL of 70% perchloric acid and 5 mL of 65% nitric acid. The contents were heated on a hot plate at 200°C until the solution become clear (1 h), then the acid was evaporated to dryness. The residue was dissolved in 5 mL of 1.0-M $HNO_3$ and transferred to a 100-mL, calibrated volumetric flask, and diluted to the mark. Before applying the preconcentration procedure, the pH of these solutions was adjusted by sodium hydroxide solution.

## Apparatus

The determination of copper, magnesium lead, manganese, cobalt, nickel, and zinc was performed on a Varian Techtron Model 1000 atomic absorption spectrometer under the recommended conditions for each metal ion. The determinations of lithium, sodium, potassium, calcium, and barium were performed on a Jenway flame photometer Model PFP7 under the recommended conditions for each metal ion. A Metrohm E-603 digital pH meter equipped with a combined glass–calomel electrode was used for the pH adjustments.

## Sample Extraction

Extractions were performed with 47-mm diameter × 0.5-mm thickness Empore membrane disks containing octadecyl-bonded silica (8 μm particle, 60 Å pore size) from Varian. The typical composition of the disks was 90% w/w octadecyl-bonded silica and 10% w/w PTFE fibers. The disks were used in conjugation with a standard Millipore 47-mm filtration apparatus connected to a water aspirator.[19–23]

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 mL of methanol was poured onto the disk and immediately drowns through the disk by applying a slight vacuum. After all of the solvent had passed through the disk, it was dried by passing air through it for a few minutes. The disk conditioning was then begun by pouring 10 mL of methanol onto the disk. Immediately, a low vacuum was applied and the solvent was drown through the disk until solvent surface almost reached the surface of the disk. The disk should not be allowed to soak without vacuum, and any air should not be allowed to contact with the surface of the disk.

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Then, a solution of 8 mg of AQ dissolved in 10 mL of methanol was introduced onto the disk and was drawn slowly through the disk by applying a slow vacuum. The passed solution was collected in a test tube. Then 5 mL of water was added to the test tube and the resulting colloidal solution was again introduced to the reservoir and passed through the disk slowly. The filtration step was repeated until the passed solution was completely clear. Finally, the disk was washed with 25 mL of water and dried by passing air through it. The membrane disk modified by AQ was now ready for sample extraction.

The general procedure for the extraction of $Cu^{2+}$ ions on the membrane disk was as follows. The modified disk was first washed with 5.0 mL of a 1 : 1 methanol–water mixture followed by washing with 10 mL of water. This step pre-wets the surface of the disk prior to the extraction of $Cu^{2+}$ ions from water and ensures a good contact between the analyte and the ligand. It is important to note that the surface of the disk was not left to become dry after pre-wetting step until the extraction of $Cu^{2+}$ ions from water was completed. The disk was then conditioned with 25 mL of a 0.1-M buffer solution with the same pH as the sample solution. Then, 500 mL of sample solution containing 10 mg $Cu^{2+}$ at pH was passed through the membrane (flow rate = 25 mL $min^{-1}$). After the extraction, the disk was dried completely by passing air through it for a few minutes. The extracted copper was stripped from the membrane disk using 3 mL of 0.1-M nitric acid (by applying a slight vacuum). The eluted solution was collected in a test tube and transferred into a 5-mL calibrated flask. The test tube was washed with another 1-mL portion of 0.1-M $HNO_3$ and added to the flask. The flask was finally diluted to the mark with 0.1-M nitric acid. All working standard solutions of $Cu^{2+}$ ion were prepared in 0.1-M nitric acid.

## RESULTS AND DISCUSSION

9,10-Anthraquinones are well known to form fairly stable complexes with such transition metal ions as $Pb^{2+}$ and $Cu^{2+}$. The anthraquinone AQ bearing two hydrophobic $\pi$-donating arms is insoluble in water at neutral pH. Our recent spectrophotometric studies revealed that AQ forms a very selective and stable 1 : 1 complex with $Cu^{2+}$ ion.[34] We thus decided to examine its capability as a suitable reagent for the preconcentration and separation of $Cu^{2+}$ ions via SPE, by using octadecyl-bonded silica membrane disks.

Some preliminary experiments were carried out to investigate the quantitative retention of copper ions by the membrane disks in the absence and presence of AQ, after the recommended washing, wetting, and conditioning procedures were carried out. It was found that while the conditioned membrane disk itself retained only about 5% of $Cu^{2+}$ ions, the membrane disk

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modified by AQ was capable of retaining the copper ions in the sample solution quantitatively (the test solution contained 10 μg of copper in 500 mL of water at pH 7.0).

The optimal amount of AQ that must be adsorbed on the octadecyl silica membrane disks for the quantitative recovery of 10 to 50 μg of copper from aqueous sample solutions was investigated (Table 1). It was found that the extraction of copper is quantitative using 8 mg on more of the ligand.

To choose a proper stripping acid solution, the retained $Cu^{2+}$ ions, after the quantitative extraction of 10 μg of copper from a 500-mL solution by disks modified with 10 mg of AQ, were stripped from the disk with different volumes of varying concentrations of different acids. The results are summarized in Table 2. As is obvious, the lower the acid concentration used, the higher the volume necessary for the quantitative elution of the retained copper ions. As is seen from Table 2, 3 mL of 0.1-M solutions of nitric acid, sulfuric acid, and hydrochloric acid can afford the quantitative stripping of the retained copper(II) from the modified disks. Since the nitrate ion is reported to be a more acceptable matrix for both flame and electrothermal AAS experiments than chloride and anions of other acids used,[5] 3 mL of 0.1-M nitric acid was used as eluent for further studies.

It is interesting to note that both the adsorption and stripping steps of copper(II) on the modified membrane disks can also be easily realized by an intense change in the color of the disks. Adsorption of copper ions by the modified disk immediately changes its color from an orange color to a deep-red color. On the other hand, stripping of copper ion from the modified disks upon addition of 3 mL of 0.1-M $HNO_3$ is associated with an immediate intense change in the disk's color from dip-red to orange.

***Table 1.*** Percent recovery of copper(II) from the membrane disks modified with different amounts of AQ.[a]

| Amount of AQ (mg) | Recovery (%) |
|---|---|
| 0.0 | 5 |
| 2.5 | 50 |
| 5.0 | 86 |
| 7.5 | 100 |
| 10.0 | 100 |
| 12.5 | 100 |

[a]Initial samples contained 10 μg $Cu^{2+}$ in 500 mL water.

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***Table 2.*** Percent recovery of copper(II) from the modified membrane disks using different stripping acid solutions.

| Stripping acid | Concentration (M) | Recovery (%) | | | |
|---|---|---|---|---|---|
| | | 3[a] | 5[a] | 10[a] | 15[a] |
| $HNO_3$ | 0.005 | — | 0 | 3 | 10 |
| | 0.01 | — | 25 | 7 | 100 |
| | 0.1 | 100 | 100 | 100 | 100 |
| $H_2SO_4$ | 0.005 | — | 11 | 39 | 68 |
| | 0.01 | — | 48 | 100 | 100 |
| | 0.1 | 100 | 100 | 100 | 100 |
| HCl | 0.005 | — | 3 | 30 | 58 |
| | 0.01 | — | 24 | 76 | 100 |
| | 0.1 | 100 | 100 | 100 | 100 |
| $CH_3COOH$ | 0.01 | — | 0 | 4 | 12 |
| | 0.1 | — | 48 | 100 | 100 |

[a]Volume (mL).

Most chelating ligands are conjugate bases of weak acid groups and, accordingly, have a very strong affinity for hydrogen ions. The pH, therefore, will be a very important factor in the separation of metal ions by chelation, because it will determine the values of conditional stability constants of the metal complexes on the surface of the sorbent.[35] Due to the presence of a hydroxy group on the AQ structure, it is expected that the extent of its complexation is sensitive to pH.[33,34] Thus, the effect of pH on the extraction of copper ions was studied.

To investigate the effect of pH on the SPE of copper(II) ion, the membrane disk was modified with 12 mg of AQ and the pH of 500-mL aqueous samples containing 10 μg $Cu^{2+}$ was varied from 4.0 to 7.5, using appropriate buffer solutions. The resulting percent recoveries vs. pH of solution are shown in Table 3. As is seen, the percent recovery of $Cu^{2+}$ ion increases with increasing pH of solution until a pH of about 6.5 is reached. Quantitative extraction of copper ion occurs at a pH range of 6.5 to 7.2. pH values higher than 7.5 were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks.[19] Thus, a buffer solution of pH 7.0 was adopted for further studies.

The maximum capacity of the membrane disk modified by 8 mg of AQ was determined by passing 1000-mL portions of an aqueous solution containing 1000 μg of copper at pH 7.0, followed by the determination of retained metal ions using AAS. Maximum capacity of the membrane disk was found to be $440 \pm 20$ μg of $Cu^{2+}$ ion on the disk.

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***Table 3.*** Effect of pH of test solution on the recovery of 10 μg copper(II) from 500 mL water.

| pH of solution | Recovery (%) |
|---|---|
| 4.1 | 23.5 |
| 4.5 | 24.0 |
| 5.0 | 36.0 |
| 5.6 | 58.5 |
| 6.0 | 81.0 |
| 6.5 | 98.5 |
| 6.6 | 99.5 |
| 6.7 | 99.5 |
| 7.0 | 100.0 |
| 7.2 | 100.0 |

The breakthrough volume of sample solution was tested by dissolving 10 μg of copper in 100, 250, 1000, 1500, 2000 mL of water and the recommended procedure was followed under optimal experimental conditions. In all cases, the extraction by membrane disk was found to be quantitative. Thus, the breakthrough volume for the method should be greater that 2000 mL. Consequently, by considering the final elution volume of 5.0 mL and the break through volume of 2000 mL, an enrichment factor of 400 was easily achievable.

The limit of detection (LOD) of the proposed method for the determination of copper(II) was studied under the optimal experimental conditions. The LOD obtained from $C_{\mathrm{LOD}} = K_b S_b / m$[36] for a numerical factor $K_b = 3$ is 100 ng per 1000 mL.

To investigate the selective separation and determination of $Cu^{2+}$ ion from its binary mixtures with diverse metal ions, an aliquot of aqueous solution (500 mL) containing 10 μg of copper(II) ion and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table 4. The results clearly indicate that 10 μg of $Cu^{2+}$ ions in the binary mixture is retained almost quantitatively by the modified membrane disk, even in the presence of 5000 mg of diverse ions.

To assess the applicability of the method to real samples, it was applied to the recovery of copper(II) ions from a 500-mL synthetic seawater sample and to the preconcentration and determination of copper(II) from SRM bovine liver and tea leaves. The results are summarized in Table 5. As is obvious, the copper content of the samples can be quantitatively recovered from their

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*Table 4.* Recovery of copper from binary mixtures.[a]

| Diverse ion | Amount taken (mg) | Percentage recovery of $Cu^{2+}$ ion |
|---|---|---|
| $Na^{+}$ | 5000 | 99.6 (0.6)[b] |
| $Li^{+}$ | 20 | 99.3 (1.6) |
| $K^{+}$ | 200 | 98.3 (1.8) |
| $Mg^{2+}$ | 600 | 100.5 (1.1) |
| $Ca^{2+}$ | 200 | 97.9 (1.9) |
| $Sr^{2+}$ | 20 | 99.2 (0.2) |
| $Ba^{2+}$ | 20 | 98.5 (1.2) |
| $Pb^{2+}$ | 1 | 100.4 (1.0) |
| $Ni^{2+}$ | 3 | 100.6 (1.8) |
| $Co^{2+}$ | 3 | 97.8 (1.6) |
| $Mn^{2+}$ | 0.5 | 99.4 (2.1) |
| $Zn^{2+}$ | 1 | 97.2 (1.3) |

[a]Initial samples contained 10 μg $Cu^{2+}$ and different amounts of diverse ions in 500 mL water.
[b]Values in parentheses are RSDs based on three replicate analyses.

matrices. There is also a satisfactory agreement between the results obtained by the proposed method and those by the ICP method.

## CONCLUSION

In this work, trace amounts of $Cu^{2+}$ ion in aqueous samples were selectivity preconcentrated on octadcyl silica membrane disks modified with a 9,10-anthraquinone derivative having two propenyl arms, and determined by FAAS. The novelty of the proposed method, as compared with the current published reports,[5–9,11,12,15] lies in its ease of operation, relatively fast procedure, very high enrichment factor of 400, very low limit of detection of 0.1 ng per mL, and,

*Table 5.* Determination of copper in different samples.

| | Copper concentration | |
|---|---|---|
| Sample | SPE | ICP |
| Synthetic seawater | $9.82 \pm 0.14\ \mu g\ mL^{-1}$ | $10.01 \pm 0.05\ \mu g\ mL^{-1}$ |
| Tea leaves | $0.207 \pm 0.005\ \mu g\ g^{-1}$ | $0.210 \pm 0.003\ \mu g\ g^{-1}$ |
| SRM bovine liver | $153 \pm 4\ \mu g\ g^{-1}$ | $158 \pm 7\ \mu g\ g^{-1}$ |

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especially, high selectivity. The method can be successfully applied to the preconcentration and determination of copper in different real samples.

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