Full Paper

Determination of Ultra Trace Copper in Water Samples by Differential Pulse Polarography after Solid Phase Extraction

Mahmood Payehghadr[*] and Farzaneh Nourifard

Department of Chemistry, Payame Noor University, 19395-3697 Tehran, Iran.

Abstract: A high selective and sensitive anodic stripping differential pulse polarographic method for determination of ultra-trace amounts of Cu^{2+} ion in water samples is proposed. The method is based on the separation and preconcentration of Cu^{2+} on an octadecyl bonded silica (ODBS) membrane disk modified by a recently synthesized triazene ligand, ([1-(ortoacyl benzene)3-(3,4-dichlorobenzene)triazene]). Various parameters such as, pH of aqueous solution (7-8), flow rates (10 mL min^{-1}), the amount of ligand (6.0 mg) and the type of stripping solvent (0.1M nitric acid) have optimized. The breakthrough volume was greater than 500 mL with an enrichment factor of more than 100 and 3.88µg L^{-1} detection limit. The capacity of the modified disks is 220µg of copper per 6mg of the ligand. The effects of various cationic interferences on the percent recovery of copper ion were studied. The method was successfully applied to the determination of copper ion in different samples.

Keywords: copper (II); SPE; stripping voltammetry

1. INTRODUCTION

Recently, the structural and solution studies of triazene ligands [1-3], application of these compounds as a selective modifier for solid phase extraction and determination of toxic metal ions [4-5], potentiometric sensor [6-7], Hg (II) and Pt (II) ion selective electrodes [8] have been reported.

Copper is widespread anthropogenic pollutant of environment and the determination of this metal ion is an actual problem [9]. The determination of copper is usually carried out by flame [10-11] and graphite furnace [12] atomic absorption spectrometry, as well as spectrophotometry [13], chemiluminescence [14], electrothermal and electroanalytical methods [15]. However, due to presence of copper in low levels in environmental samples and the matrix effects, different separation and preconcentration techniques such as liquid-liquid extraction [16], liquid-liquid micro extraction [17], precipitation [18-19], ion exchange [20], solid phase extraction [21-22] and membrane filtration [23] improve the analytical detection limit, increase the sensitivity by several orders of magnitude, enhance the accuracy of the results and facilitate the calibration. Among these techniques, solid phase extraction is preferred by many researchers and account of the fast, simple and higher preconcentration factor, rapid phase separation, time and cost saving and on-line using [24-25].

Liquid–liquid extraction of copper with organic solutions containing different chelating agents such as dithiocabamates and macrocyclic ligands has attracted considerable attention. However, these classical extraction methods are usually time-consuming, labor-intensive and require large volumes of high purity organic solvents. In recent years, different trapped ligands on a variety of solid matrices have been successfully used for the preconcentration, separation and sensitive determination of trace metal ions [26].

Solid phase extraction (SPE) is an attractive technique that reduces consumption of and exposure to solvent, disposal costs and extraction time. Solid-phase extraction has advantages over other preconcentration methods in terms of simplicity, economy, rapidity, reusability of the adsorbent; ease of automation, higher preconcentration factor, lower consumption of reagents, and more importantly its

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[*]Corresponding author. E-mail: mahmood_payehghadr@yahoo.com

environmental friendliness (use of less organic solvents). The most extensively used SPE sorbents are modified C18 Silica [27], activated carbon [28], alumina [29] and Amberlite XAD resins [30]. For example, silica and silica bonded adsorbents offer good advantages in terms of thermal, mechanical and chemical stability. In addition, they act selectively towards a particular metal ion. In fact, the modified silica gel surfaces are known to act as a weak cation exchanger via its weak silanol groups, through immobilization of organic complexing agents, either chemically or physically. These modified surfaces greatly enhance metal exchange capacity and improve selectivity of these phases to metal ion removal, separation or preconcentration prior to their determination by x-ray fluorescence or AAS analysis [31].

Anodic stripping differential pulse polarography is a sensitive technique for the determination of trace amount Cu^{2+} in aqueous media. This technique reduces consumption and exposure to solvent, disposal costs, and extraction time. Octadecyl bonded silica (ODBS) membrane disks have been utilized for the extraction and analysis of many different organic and environmental matrices. Moreover, these membrane disks modified by suitable ligands are successfully used for the separation and sensitive determination of metal ions [32-33].

In this work, preconcentration of ultra trace copper (II) in aqueous media using octadecyl silica membrane disks modified by a recently synthesized triazene (Fig. 1) and determination by anodic stripping differential pulse polarography have been reported. Different experimental conditions, e.g. the type and volume of eluting solvent, the effect of pH, the effect of sample and eluent flow rates and the amount of ligand, on the extraction efficiency and breakthrough volume, limit of detection and maximum capacity of the disks for Cu^{2+} ion recovery have been studied.
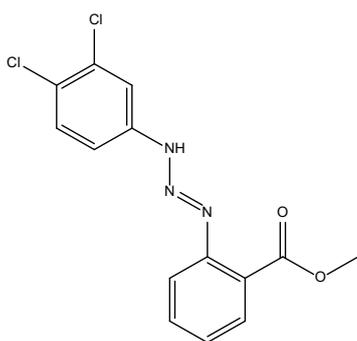

Figure 1. The [1-(ortoacyl benzene)3-(3,4-dichlorobenzene)triazene] ligand

2. MATERIAL AND METHODS

Reagents

Extra pure methanol, acetonitrile, nitric acid, hydrochloric acid, acetic acid, sulfuric acid and perchloric acid (all from Merck) were used as received. The nitrate or chloride salts of the cations (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying.

The ligand synthesized, purified and dried as it has been described elsewhere [1]. Doubly distilled deionized water was used throughout. The standard stock solution of copper (II) (1000 ppm) was prepared by dissolving1.0000 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 appropriate dilution of the stock solution with water. 0.1 M acetate and phosphate buffer solutions were used for the pH ranges 4.0–5.5 and 6.0–7.5, respectively.

Apparatus

The determinations of copper were performed on a Metrohm 797 polarograph. A Metrohm E-603 digital pH meter equipped with a combined glass calomel electrode was used for the pH adjustments. The modified C18 extraction disks were used in conjunction with a standard 47 mm filtration apparatus (Schleicher and Schüell, Dassel, Germany) connected to a vacuum.

Sample extraction

Extractions were performed with 47 mm diameter×0.5mm thickness Empore membrane disks containing octadecyl-bonded silica (8 µm particles, 60Å pore size) from 3M Company. The typical composition of the disks was 90% w/w octadecyl bonded silica and 10% w/w PTFE fibers. The disks were used in conjunction with a standard Millipore 47 mm filtration apparatus connected to vacuum.

In order 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 methanol was poured onto the disk and immediately drowns through the disk by applying a slight vacuum. After all of the solvent has passed through the disk, it was dried by

passing air through it for few minutes. The disk conditioning was then begun by pouring 10 mL methanol on to the disk. Immediately a low vacuum was applied and the solvent was drowning through the disk until solvent surface almost reaches 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. Then, a solution of 5 mg of ligand dissolved in 5 mL acetonitrile 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 2 mL water was added to the test tube and the resulting colloidal solution was again introduced to the passed through the disk slowly. The filtration step was repeated until the passed solution was completely clear. Finally, the disk was washed with 25mL water and dried by passing air through it. Thus, the membrane disk modified by the ligand is 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 0.5 mL methanol followed by washing with 25 mL water. This step prewets 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 from the time methanol was added 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 100 mL of sample solution containing 10 μg Cu^{2+} at optimum pH was passed through the membrane (flow rate =10 mL min^{-1}). After the extraction, the disk was dried completely by passing air through it for a few min. The extracted copper was stripped from the membrane disk using 5mL of 0.1 M nitric acid by applying a slight vacuum.

The eluted solution was collected in a test tube and then transferred into a 10 mL calibrated flask. The test tube was washed with another 1 mL portion of 0.1 M HNO_3 and added to the flask. Finally, the flask was diluted to the mark with 0.1 M nitric acid. All working standard solutions of Cu^{2+}ion were also prepared in 0.1 M nitric acid.

3. RESULTS AND DISCUSSION

Choice of effluent

In order to choose a proper effluent for the

retained Cu^{2+} ions, after the extraction of 10 μg copper from 100 ml water by the modified disks, the copper ions were stripped with different volumes of varying concentration of different acids and others solvent (Table 2). From the data given in Table 1 it is immediately obvious that, while 5ml of the 0.1 M mineral acids can accomplish the quantitative elution of copper from the membrane disk, 5ml nitric acid can do the job better. As is also obvious, the lower the acid concentration used, are suitable for the quantitative elution of the retained copper ions. Thus, 5 mL of 0.1M HNO_3 was used as effluent for further studies.

Table 1. Percent recovery of cu^{2+} from the modified membrane disk using different stripping solution.

Stripping solution	% Recovery Cu^{2+}
HNO_3 (0.1 M)	100
HCl (0.1 M)	64.8
H_2SO_4 (0.1 M)	100
HNO_3 (0.5 M)	100
HCl (0.5 M)	65
H_2SO_4 (0.5 M)	100
EDTA (0.1 M)	71.1
NH_4SCN (0.1 M)	2.2

Effect of pH

The effect of pH on the extraction of copper ions was studied. In order to investigate the effect of pH on the SPE of copper (II) ion, the membrane disk was modified with 6mg of ligand and the pH of aqueous samples containing 10μg $Cu^{2+}$was varied from 4.0 to 8, using appropriate buffer solutions. The resulting percent recovery versus pH plot is show in Figure 2. As seen, the percent recovery of Cu^{2+} ion increases with increasing pH of solution until a pH of about 7 is reached. Quantitative extraction of copper ion occurs at a pH range 7–8. The pH values higher than 8 were not tested. Thus, a buffer solution of pH 7.0 was adopted for further studies.

Effect of ligand amount

As the amount of loaded ligand on the membrane disk increases, the flow rate of solutions through the modified disk will decrease. Thus, the least amount of ligand necessary for the quantitative extraction of 10 μg Cu^{2+} from a 100 mL aqueous sample at pH 7.0 was studied. The results are shown in Figure 3. As seen, the extraction of copper is quantitative using above 6 mg of ligand. Hence,

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subsequent extraction experiments were carried out with 6mg of the ligand. As seen, the extraction of copper decrease with 8mg ligand.
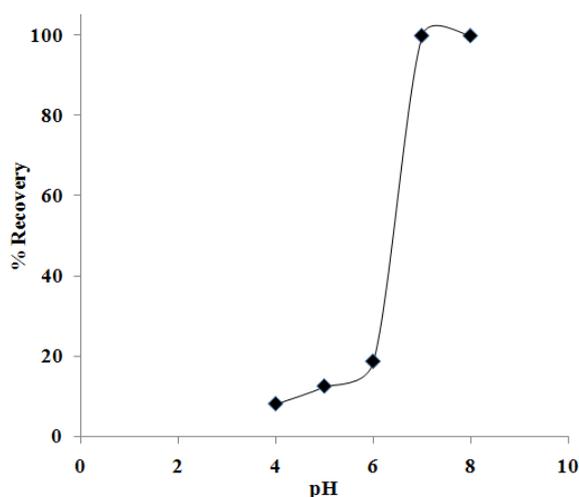

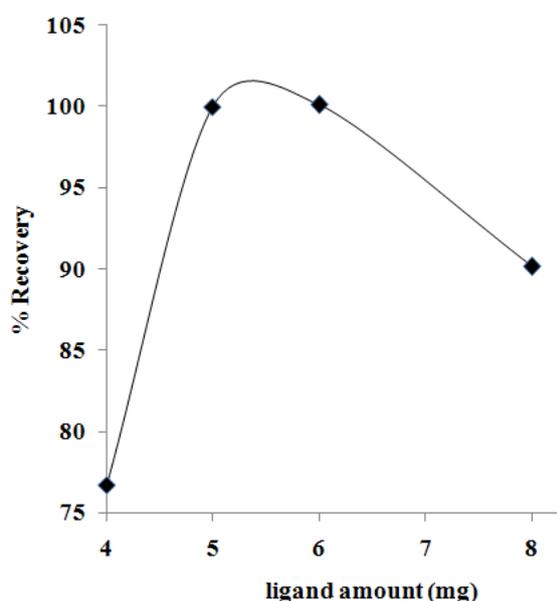**Figure 2**. The effect of pH of the sample on extraction recovery of Cu^{2+} ion.

Figure 3. Effect of amount of the ligand on extraction recovery of Cu^{2+} ion.

Effect of flow rate

The effect of flow rates of the sample and stripping solutions from the modified membrane disk on the retention and recovery of copper (II) was investigated. It was found that, in the range of 5-30mL min^{-1}, the retention of copper by the membrane disk is affected the sample solution flow rate considerably. On the other hand, quantitative

stripping of Cu^{2+} ions from the disk was achieved in a flow rate range of 10 ml min^{-1}, using 5 ml of 0.1 M nitric acid. At higher flow rates, quantitative stripping of copper decreased the recovery.

Analytical performance

The maximum capacity of the membrane disk modified by 6 mg ligand was determined by passing 500 ml portions of an aqueous solution containing 300μg copper at pH 7.0, followed by the determination of retained metal ions using anodic stripping differential pulse polarography. The maximum capacity of the membrane disk was found to be 220μg of Cu^{2+} ion on the disk.

The breakthrough volume of sample solution was tested by dissolving 10 μg of copper in 100, 250, 500, and 1000 mL water and the recommended procedure was followed under optimal experimental conditions. In all cases, the extraction by the membrane disk was found to be quantitatively. Thus, the breakthrough volume for the method should be greater than 500 mL. Consequently, by considering the final elution volume of 5.0 mL and the breakthrough volume of 500mL, an enrichment factor of 100 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. Figure 4 (a and b) illustrated a series of recorded polarograms responses with increasing the concentrations of Cu^{2+}. As shows figure 4(b), the peak currents have a good linear relationship with the concentration of Cu^{2+} with the linear correlation coefficients of 0.9997.The LOD obtained from $C_{LOD}=K_b S_b/m$ for a numerical factor $K_b=3$ is 3.88 μg L^{-1}.

In order to investigate the selective separation and determination of Cu^{2+}ion from its binary mixtures with diverse metal ions, an aliquot of aqueous solution (100 mL) containing 10 μg $Cu^{2+}$and different amounts (mg) of other cations was taken and the recommended procedure was followed and the results are summarized in Table 2. The results clearly indicate that 10 μg of copper (II) ions in the binary mixtures are retained almost quantitatively by the modified membrane disk, even in the presence of up to about 19.66 mg of the diverse ions.

In order to assess the applicability of the method to real samples, it was applied to the

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separation and recovery of copper (II) ions from100 ml of three different water samples and a synthetic sample. In all case, the copper (II) ions added can be quantitatively recovered from the water and synthetic matrices.
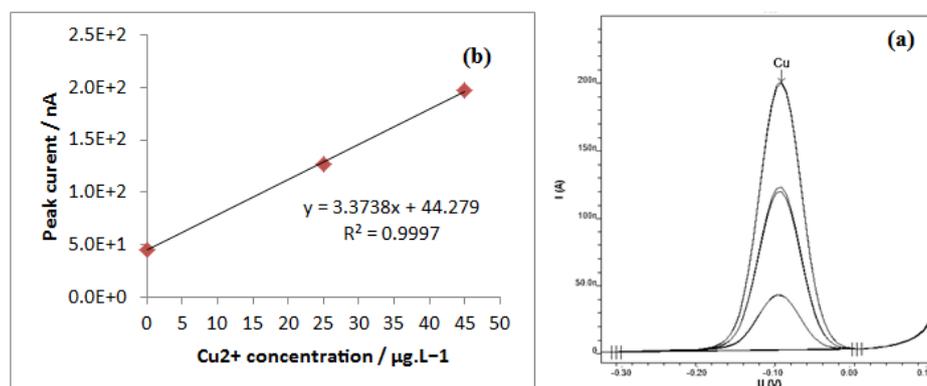

Figure 4. (a) Recorded polarograms for additions of solutions with different concentrations (from bottom to top: 0, 25 and 45 $\mu g.L^{-1}$ of Cu^{2+}, (b) The calibration curve, buffer at pH = 7.0, potential range: -0.2 to 0.0V.

Table 2. Separation of copper from binary mixtures. The initial solution contained 10 μg copper and different amount of diverse ion in 100 mL

Diverse ion	Amount taken, mg	Recovery of Cu^{2+}
Zn^{2+}	0.44	100
Ni^{2+}	7.05	100
Pb^{2+}	1.87	100
Ba^{2+}	7.04	90.0
Ca^{2+}	2.91	97.3
Mg^{2+}	3.06	77.0
K^+	8.73	89.8
Na^+	19.66	92.5
Hg^{2+}	0.618	50.1

4. CONCLUSION

A high selective and sensitive anodic stripping differential pulse polarographic method have reported for determination of ultra-trace amounts of Cu^{2+} ion in water samples.

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