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Solid Phase Extraction of Ultra Trace Copper(II) Using Octadecyl Silica Membrane Disks Modified by Phendion Schiff Base

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A simple and reproducible method for the rapid extraction and determination of trace amounts of copper(II) ions using octadecyl-bonded silica membrane disks modified by phendion. The method is based on complex formation on the surface of the ENVI-18 DISK^{TM} disks followed by stripping of the retained species by minimum amounts of appropriate organic solvents. The elution is efficient and quantitative. The effect of potential interfering ions, pH, ligand amount, stripping solvent and sample flow rate were also investigated. Under the optimal experimental conditions, the break-through volume was found to about 1000 mL providing a preconcentration factor of 500. The maximum capacity of the disks was found to be 455 ± 5 µg for Cu^{2+}. The limit of detection of the proposed method is 3 ng per 1000 mL. The method was applied to the extraction and recovery of copper in different water samples.

Key Words: Copper(II), SPE, Octadecyl slica disks, Atomic adsorption spectrometry, Phendion.

INTRODUCTION

Copper(II) at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems[1-8]. This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, copper can bind to the cell membrane and hinder the transport process through the cell wall. Copper at nearly 40 ng mL^{-1} is required for normal metabolism of many living organisms[9,10]. On the other hand, copper is an important element in many industries. Thus, the development of new methods for selective separation, concentration and determination of copper(II) in sub-micro levels in different industrial, medicinal and environmental samples is of continuing interest. The determination of copper is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS)[11,12] as well as spectrometric methods[13,14]. However, due to the presence of copper(II) in medicinal and environmental samples at low levels, its separation from other elements presents and also the use of a preconcentration step prior to its determination is usually necessary.

Different methods, especially liquid-liquid extraction of copper(II) 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, labour-intensive and requires large amounts of high purity solvents for extraction. Nevertheless, several other techniques for the preconcentration and separation of copper(II) 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[28,29], 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 popular 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 purpose[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].

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 to develop 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 phendion and AAS determination.

EXPERIMENTAL

All acids were of the highest purity available from Merck and were used as received. Methanol and chlorofom were of HPLC grade from Merck. Analytical grade nitrate salts of lithium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt and copper were of the highest purity. Ultra pure organic solvents were obtained from E.Merck, Germany and high purity double distilled deionized water was used throughout the experiments.

The stock standard solution of Cu^{2+} was prepared by dissolving 0.1000 g of the copper powder in 10 mL conc. nitric acid and diluted to 1000 mL with water in a calibrated flask. Working solutions were prepared by appropriate dilution of the stock solution.

Characterization of phendion: The phendion Schiff base was synthesized according to the reported method[46]. The speciation of the yellow crystals obtained as product were: m.p. 124-127 °C; 1.9 g, yield 90 % ; IR (KBr, ν_{max}, cm^{-1}): 3200 and 3190, 1610, 1570, 1492, 1425, 1352, 1250, 1112, 1001, 877, 755; MS, m/z (%): 211(M^+, 59). Anal. Calcd. for $C_{12}H_7N_2O_2$ (m.w. 211.21).

Determination of Cu^{2+} contents in working samples were carried out by a Varian spectra A-200 model atomic absorption spectrometer equipped with a high intensity hallow cathode lamp (HI-HCl) according to the recommendations of the manufacturers. These characteristics are tabulated in Table-1.

TABLE-1
OPERATIONAL CONDITIONS OF FLAME FOR DETERMINATION OF COPPER

Slit width	0.7 nm
Operation current of HI-HCl	15 mA
Resonance fine	324.8 nm
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	7.0 mL min^{-1}
Acetylene flow	1.7 mL min^{-1}

Solid phase extractions were carried out by glassy membrane disks, ENVI-18DISK™ 47 mm diameter × 0.6 mm thickness containing octadecyl silica bonded phase (30 µm particles, 70 Å pore size) obtained from supelco in conjunction with a standard Millipore 47 mm filtration apparatus equipped with a vacuum pump. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

Sample extraction: Extraction were performed with glassy membrane disks, ENVI-18 DISK™ 47 mm diameter × 0.6 mm thickness containing octadecyl silica bonded phase (30 µm particles, 70 Å pore size) from Supelco. The disks were used in conjunctions with a standard Millipore 47 mm filtration apparatus connected to water aspirator[47].

Sample treatment: The water samples were filtered through 45 µm nylon filters. Sampling vessels were polyethylene bottles soaked in 1 mol L^{-1} HNO_3 overnight and rinsed twice with deionized water. The analysis must be done within 2 d of sample collection to limit the risk of inter conversion of copper(II). Then, 5 mL of methanol was added to a 90 mL portion of each before analysis. The surface of ENVI-18 DISK™ disks is not modified with phendion and therefore could not retain Cu^{2+} ions properly. Instead, 10 mg of phendion was dissolved in an appropriate volume of an organic solvent (5 mL) miscible with water. The most suitable solvent under the experimental conditions was acetone. The phendion solution was added to aqueous solution of Cu^{2+} and the mixture was stirred gently.

Disk cleaning and conditioning: A disk was placed in the apparatus and was washed with 10 mL of methanol to remove all contaminants arising from the manufacturing process and the environment. Then, the disk was dried by passing air through it for several minutes. To ensure optimal extraction of the analytes of interest, the disk was again washed with 10 mL of methanol, immediately followed by 10 mL of water, without letting the surface of the disk dry. This step pre-wets the disk surface prior to extraction. Improper performance of this step causes slow flow-rate and poor analyte recoveries. It is important to avoid any air contact with the surface of the disk before the addition of the sample.

Sample addition: After complete homogenization, accurate volumes of the sample solutions (100 mL portions) were transferred to the top reservoir of the disk apparatus. At the same time, the solution was drawn through the disk by applying a mild vacuum. Application of vacuum was continued until the disk was completely dry (*ca.* 5 min).

Analyte elution: In order to elute the analyte selectively, exactly 5 mL of acidified solvents 0.1 M HCl in methanol was passed through the disk and collected into a 5.0 mL volumetric flask under the extraction funnel. It was found that ultra pure alcoholic organic solvents were the best eluting agents. The concentration of copper(II) in the eluates were then determined by FAAS using an external calibration graph.

RESULTS AND DISCUSSION

Some preliminary experiments were performed for investigation of absence or presence of TEBD on the quantitative extraction of copper(II). It was concluded that the membrane disk itself does not show any tendency for the retention of copper(II), but introduction of 100 mL portions of aqueous copper(II) samples containing 10 µg of copper(II) and 10 mg of phendion leads to satisfactory its retention (Table-2). The latter

TABLE-2
EFFECT OF PRESENCE OF PHENDION ON EXTRACTION PERCENT OF COPPER(II)[a]

Phendion	pH	Extraction of copper(II) (%)
Absent	2-6	0.04(7.9)[b]
Present	2-6	99.2(1.9–87(2.1)

[a] Initial samples contained 10 µg of copper(II) in 100 mL of water.

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

case is most probably attributed to the existence of a considerable interaction between copper(II) and the phendion. It should be mentioned that formation of stable complexes between copper(II) and phendion at pH = 2 is probably due to an ion pair formation mechanism. However, at pH higher than 2 the retention and percentage recovery of copper(II) is negligible.

Choice of eluent: In order to select the most appropriate eluent for the quantitative stripping of the retained copper(II) on the disks, 5 mL of various non organic (each containing 10 % v/v methanol) and different organic solvents were tested. The results tabulated in Table-2. As can be seen, the best eluting solvents were found to be 5 mL of methanol or ethanol, resulting in quantitative elution of copper(II) from the disk. It should be emphasized that presence of methanol in any kind of employed solvents helps to better the contact of eluent with hydrophobic surface of the disk.

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 acetate-acetic acid or sodium dihydrogen phosphate-disodium hydrogen phosphate and then solutions passed through the disks.

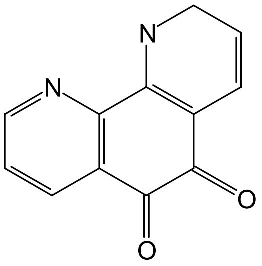

Fig. 1. Molecular structure of phendion

Eventually, the metal ions were stripped by pure methanol or ethanol solutions followed by flame atomic absorption determination of the eluted copper(II).Then, percentage recovery at various pH values was determined (Fig. 2). According to the results shown in Fig. 2, 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 phendion occurs and there is a weak tendency for retention between Cu(II) and phendion, whereas at higher values (pH > 5), Cu(II) reacts with hydroxide ions to produce $Cu(OH)_2$. Therefore, sodium acetate-acetic acid buffer with pH = 5 was used for the preconcentration step. Other solvents used for dissolving phendion were methanol and ethanol. The influences of these solvents on the recoveries as a function of pH are compared (Fig. 2). Meanwhile, 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 in the disks[48].

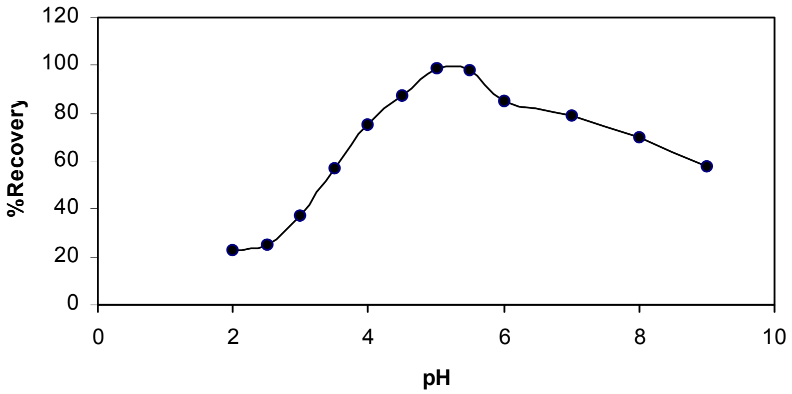

Fig. 2. Influence of sample pH and dissolving solvent of phendion on the percentage recovery of Cu(II)

TABLE-3
EFFECT OF DIFFERENT ELUTING SOLVENTS ON PERCENTAGE RECOVERY OF COPPER(II) ADSORBED ON THE DISK[a]

Stripping solution	Recovery (%)		
	2 mL	5 mL	10 mL
Methanol	84(2.6)[b]	98.9(1.9)	99.7(2.0)
Acidified methanol [c]	57(2.1)	78.6(2.2)	87.5(2.0)
Ammonical methanol[d]	59(2.1)	87.7(2.7)	86.9(2.2)
Ethanol	89(1.7)	99.4(1.8)	99.0(1.7)
1-Propanol	43(4.6)	55.0(5.5)	68.0(5.9)
Formic acid (1 M) 10 % v/v methanol	57(1.2)	77.0(1.0)	79.0(1.2)
Acetonitrile	59(1.8)	87.0(2.0)	90.0(1.5)
Hydrochloric acid (1 M) 10 % v/v methanol	57(2.0)	87.0(1.9)	90.0(1.5)
Nitric acid (2 M) 10 % v/v methanol	32(1.9)	47.0(2.2)	88.0(2.0)
Nitric acid (1 M) 10 % v/v methanol	30(2.1)	46.0(1.6)	77.0(1.7)
Ethanol	84(2.8)	99.7(2.0)	98.8(1.9)

[a] Initial samples contained 10 µg of each copper in 100 mL water.
[b] Values in parentheses are RSD based on five individual replicate analysis.
[c] Acidified solvents obtained by addition of 0.1 M HCl.
[d] Ammonical solvents obtained by addition of 0.1 M NH_3.

Effect amount of counter anion: In order to investigate the effect of counter ion on the recovery of Cu^{2+} ions by the modified disks, different counter anions were tested (Table-4). It is immediately obvious that the nature of the counter anion strongly influences the retention of copper ions by the disk. The results revealed that the phendion behaves as a neutral ionophore in the pH range 5.5-6.0[49,50] so that the Cu^{2+} ions are retained as ion pair complexes by the membrane disks. As seen, CH_3COO^- ion is the most efficient counter anion for the SPE of Cu^{2+} ion. The influence of the concentration of sodium acetate on copper recovery was investigated and the results are shown in Table-4. As seen, the percent recovery of Cu^{2+} increased with the acetate concentration until a reagent concentration of about 0.1 M is reached, beyond which the recovery remained quantitative.

TABLE-4
PERCENT RECOVERY OF COPPER FROM THE MODIFIED MEMBRANE DISK IN THE PRESENCE OF 0.01 M OF DIFFERENT COUNTER ANIONS[a]

Counter anion	Recovery (%)	Counter anion	Recovery (%)
Cl^-	23.9	SCN^-	18.0
Br^-	32.5	Picrate	78.8
ClO_4^-	51.9	Acetate	99.2

Moreover, acetate ion acts as a suitable buffering agent, while it effectively contributes to the ions- pair formation; thus, in the SPE experiments, there was no need for the addition of any buffer solution.

The influence of flow-rate: One of the most important parameters affecting solid phase extraction is the speed of the process. Hence, the effect of flow-rates on extraction efficiencies was investigated. It was found that in the range of 10-100 mL min^{-1}, the retention of Cu(II) was not considerably affected by the sample solutions flow-rates and leads to reproducible and satisfactory results (Fig. 3). Thus, the flow-rate was maintained at 90 mL min^{-1} throughout the experiment.

Quantity of the phendion: The optimum amount of phendion for the quantitative extraction of Cu(II) was also investigated by adding various amounts of it to solution(between 2-20 mg). The results are listed in Table-5. The experimental results revealed that the extraction of Cu(II) was quantitative using a sample solution containing more than 10 mg phendion. Hence, subsequent extractions were performed with 16 mg of phendion.

Disk efficiency: 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™ disk could perform at least 16 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 10 replicates. These observations are represented in Fig. 4.

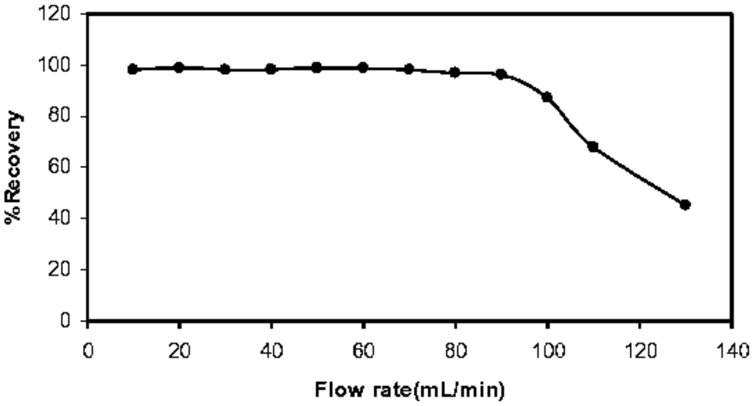

Fig. 3. The effect of the flow-rate on extraction percent of Cu(II)

TABLE-5
INFLUENCE OF THE PHENDION AMOUNT ON THE RECOVERY OF Cu(II) IONS[a]

Phendion amount (mg)	Recovery (%) of Cu(II)	Phendion amount (mg)	Recovery (%) of Cu(II)
2	55(1.8)[b]	10	96.8(1.9)
5	74(2.1)	15	99.2(1.8)
8	87(2.0)	20	98.9(1.9)

[a] Initial samples contained 10 µg of each copper in 100 mL water.

[b] Values in parentheses are RSD based on five individual replicate analysis.

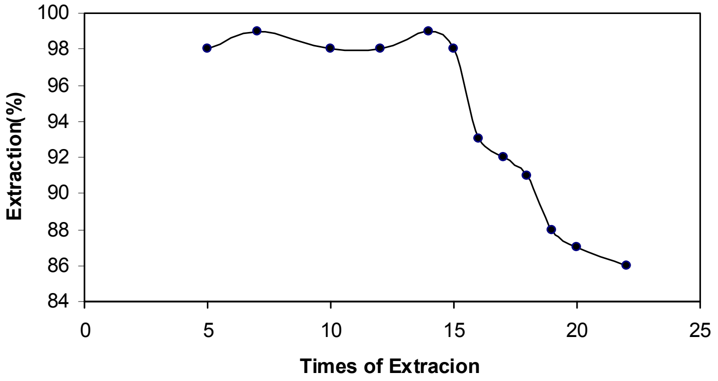

Fig. 4. Influence of eluent type on disk efficiency

Analytical performance: When solutions of 10 µg copper in 10, 50, 100, 500, 1000, 2000, 2500 and 3000 mL solutions under optimal experimental conditions were passed through the disks, the Cu(II) was quantita tively retained in all cases. Thus, the breakthrough volume for the method must be greater than 2500 mL, providing a concentration factor of > 500. The limit of detection (LOD) of the method for the determination of Cu(II) was studied under the optimal experimental conditions. The LOD based on 3σ of the blank is 3 ng per 1000 mL.

The capacity of modified disks (5 mg phendion) was determined by passing 50 mL portions of sample solutions containing 8 mg of copper and 0.1 M sodium acetate-acetic acid buffer with pH 5.5-6.0, followed by the determination of the retained metal ions in the eluting solution using AAS. The maximal capacity of the disk obtained from three replicate measurements was 455 ± 5 µg of Cu^{2+} on the disk.

In order to investigate the selective separation and determination of Cu^{2+} ions from its binary mixtures with various metal ions, an aliquot of aqueous solutions (50 mL) containing 10 µg Cu^{2+} and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table-6. The results show that the Cu^{2+} ions in binary mixtures are retained almost completely by the modified disk, even in the presence of up to about 100 mg of various ions. Meanwhile, retention of other cations by the disk is very low and they can be separated

TABLE-6
SEPARATION OF COPPER FROM BINARY MIXTURES[a]

Diverse ion	Amounts taken (mg)	Found (%)	Recovery of Cu^{2+} ion (%)
Na^{+}	93.5	1.17(1.9)[b]	98.5(1.6)
K^{+}	94.5	1.37(2.1)	98.6(1.5)
Mg^{2+}	13.7	1.70(2.8)	100.0(1.3)
Ca^{2+}	27.6	1.26(1.3)	99.6(1.4)
Sr^{2+}	3.78	2.85(2.2)	98.2(1.4)
Ba^{2+}	2.86	3.16(1.8)	98.5(1.3)
Mn^{2+}	2.88	1.75(1.9)	98.3(1.2)
Co^{2+}	2.70	1.80(2.0)	99.1(2.0)
Ni^{2+}	2.56	2.00(1.8)	98.6(1.6)
Zn^{2+}	2.41	1.97(1.8)	99.8(2.2)
Cd^{2+}	2.48	1.48(2.0)	99.2(1.8)
Pb^{2+}	2.32	2.22(1.9)	98.5(2.7)
Hg^{2+}	1.93	4.81(2.5)	97.6(1.8)
Ag^{+}	1.85	2.45(1.9)	96.8(1.6)
Cr^{3+}	1.56	2.92(2.3)	97.9(1.5)
UO^{2+}	2.56	1.80(1.1)	99.5(1.3)

[a] Initial samples contained 10 µg Cu^{2+} and different amounts of various ions in 100 mL water (0.1 M acetate ion).

[b] Values in parentheses are RSD based on five individual replicate analysis.

effectively from the Cu^{2+} ion. Its is interesting to note that, in other experiments, we found that in the presence of high enough concentrations $NH_2OH \cdot HCl$ as a suitable reducing agent (> 0.5M)[51]. No retention of the resulting single charge Cu^+ ion can occur by the modified membrane disk.

Analysis of water samples: 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, 26 January, 2006), snow water (Saveh, 6 February, 2006) and sea water (taken from Caspian sea, near the Mahmoud-Abad Shore) samples were analyzed (Table-7). As can be seen from Table-7 the added copper ions can be quantitatively recovered from the water samples used.

TABLE-7
RECOVERY OF COPPER(II) ADDED TO 1000 mL OF DIFFERENT WATER SAMPLES CONTAINING 0.1 M ACETATE AT pH = 5.5-6.0)

Sample	Cu^{2+} added (μg)	Cu^{2+} Determined (ng mL^{-1})
Tap water	0.0	1.87(1.9)[a]
	10.0	11.89(1.5)
Snow water	0.0	4.88(1.7)
	10.0	14.90(1.9)
Rain water	0.0	2.64(1.5)
	10.0	12.78(1.4)
Sea water	0.0	12.65(2.3)
	10.0	22.94(2.1)

[a] Values in parentheses are RSD based on five individual replicate analysis.

Conclusion

Results presented in this work demonstrate well the tremendous possibilities offered by the solid phase extraction of trace amounts of Cu(II) in water samples using octadecyl silica membrane disks modified by phendion and its determination by FAAS. The method developed was simple, reliable and precise for determining copper in water. Also, the proposed method was free of interference compared to conventional procedures to determine copper[52-56]. The method can be successfully applied to the separation and determination of copper in binary mixtures.

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