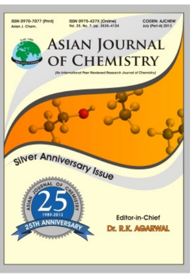
Asian Journal of Chemistry; Vol. 25, No. 9 (2013), 4983-4986

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14184



Extraction of Cu(II) Complex in Water Samples on C_{18} Modified N,N'-*Bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane and Its Determination by UV-VIS Spectrometry

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(*Received*: 7 June 2012; *Accepted*: 13 March 2013) AJC-13118

A simple method has been developed for the preconcentration of copper(II) based on the adsorption of its N,N'-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane (H_2L_2) complex on a neutral C_{18} column. The influence of acidity, eluting agents, stability of the column, sample volume and interfering ions has been investigated. The adsorbed complex could be eluted using environmentally benign polyethylene glycol (PEG 400) and the concentration of copper(II) was determined by visible spectrophotometry at 590 nm. A detection limit of 6 μg L^{-1} could be achieved and the developed procedure was successfully applied for the determination of copper(II) in spiked water samples. The preconcentration factor attainable for quantitative recovery (> 97 %) of copper(II) was 100 for a 1000 mL sample volume.

Key Words: Copper(II), Polyethylene glycol, N,N'-*Bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane.

INTRODUCTION

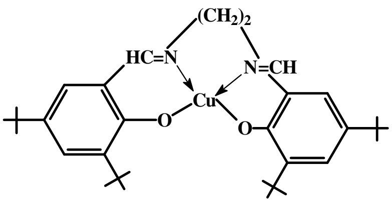
Copper at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems[1-8]. This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, copper can bind to the cell membrane and hinder the transport process through the 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 it in sub-micro levels in different industrial, medicinal and environmental samples is of continuing interest. Determination of copper is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS)[11-13] as well as spectrometric methods[14,15]. However, due to the presence of copper 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 in the presence of various classical[16-20] and macrocylic[21,22] 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[23] supercritical fluid extraction[24], flotation[25], aggregate film formation[26], liquid membrane[27], column adsorption of pyrocatechol violet-copper complexes on activated carbon[28], ion pairing[29,30], preconcentration with yeast[31] and solid phase extraction using C_{18} cartridges and disks[32-38].

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[39-41]. In recent years, the octadecyl-bonded silica solid phase extraction disks have been utilized for the extraction and separation of different organic compounds from environmental matrices[42-45]. Moreover, the solid phase extraction disks modified by suitable ligands are successfully used for selective extraction and concentration of metal ions[46,47].

In a recent series of papers[48-50], 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 complexed Cu^{2+} in low concentration.

This work preconcentration of Cu^{2+} based on the adsorption of its N,N'-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane (H_2L_2) complex on an C_{18} column. The adsorbed complex CuL_2 (**Scheme-I**) could be eluted using environmentally benign polyethylene glycol and the concentration of Cu^{2+} was determined by visible spectrophotometry. The influence of various experimental parameters such as acidity, sample volume, flow rate, diverse ions, *etc*. was examined. The validity of the proposed method was tested in spiked water samples.



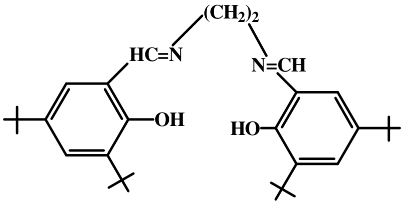
Scheme-I: Structure of complex Cu(II)- N,N'-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane

EXPERIMENTAL

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).

N,N'-*Bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane (**Scheme-II**) a was synthesized according to the procedure described by Kasumov *et al.*[51]. The tetradentate Schiff base ligands used in this work ,N,N'-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane (H_2L_2) ligands was prepared by refluxing mol of 3,5-di-*tert*-butylsalicylaldehyde and appropriate diamine in 60 mL of methanol/ethanol mixture (v/v = 3:1) for *ca*. 1 h. The products were recrystallized from methanol/$CHCl_3$ mixture (v/v = 5:1) and dried in air (yield: 80 %). The solutions were prepared using analytical grade reagents. Triple distilled water and deionized water were used for the preparation of solutions. A stock solution of 1000 µg mL^{-1} Cu(II) was prepared by dissolving 0.1354 g of copper(II) chloride (Qualigens Fine Chemicals, Mumbai, India) in 100 mL water. A working solution of 10 µg mL^{-1} was prepared by suitable dilution. About 0.01 g of N,N'-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane (H_2L_2) was dissolved in minimum amount of acetone and diluted to 100 mL. Polyethylene glycol-400 (Qualigens Fine Chemicals, Mumbai, India) solution was prepared in the ratio 7:3 by dissolving 7 mL of polyethylene glycol with 3 mL of deionized water. Neutral C_{18} (Himedia Research Laboratories, Mumbai, India) of particle size 150 mesh was used as the adsorbent. Sulphuric acid (Qualigens Fine Chemicals, Mumbai, India) of concentration 1 mol L^{-1} was prepared by diluting 55.5 mL of concentrated sulphuric acid with 1 L of de-ionized water. Water samples (Pilani, India) were collected, acidified and stored in polythene bottles.

Preparation of C_{18} column: A glass column 1.5 cm in diameter and 15 cm in length was used for the preconcentration of copper(II). About 0.8 g of neutral C_{18} was mixed with 25 mL of triple distilled water to form slurry and then loaded on to the column. Cotton was placed at the bottom for allowing C_{18} to settle properly. The column was packed up to a height of 3 cm.



Scheme-II: Structure of N,N'-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane

Procedure for preconcentration: A 1 mL volume of 10 µg mL^{-1} Cu(II) solution was mixed with 5 mL of 0.5 mol L^{-1} sulphuric acid followed by the addition of 5 mL of N,N'-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane solution and the resulting volume was maintained at 100 mL. The sample solution was loaded on to the column of neutral C_{18} maintaining a flow rate of 2 mL min^{-1}. The complex was adsorbed as a narrow band on the top of the column. The adsorbed complex was eluted using 10 mL of polyethylene glycol at a flow rate of 2 mL min^{-1} and the concentration of copper(II) was determined by visible spectrophotometry at 590 nm.

RESULTS AND DISCUSSION

Effect of acidity: The effect of acidity plays a significant role in the preconcentration studies. The volume of 0.5 mol L^{-1} sulphuric acid was varied from 1 to 6 mL in 100 mL sample volume. The results are presented in Fig. 1. Quantitative recovery (> 96 %) was obtained in the range 3.5-6.0 mL of 0.5 mol L^{-1} sulphuric acid. Beyond 6 mL, there was no change in the recovery of copper(II).

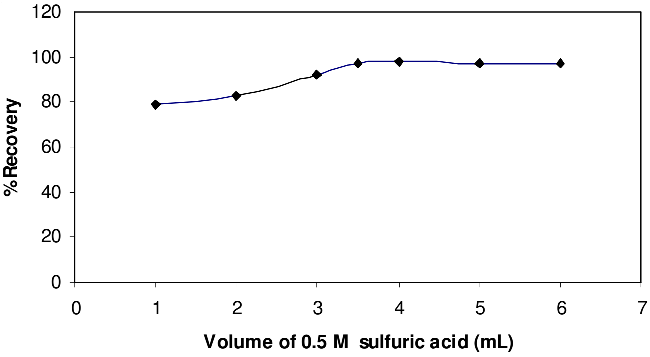


Fig. 1. Effect of variation of volume of 0.5 mol L^{-1} sulphuric acid on the recovery of copper(II)

Choice of the eluent: A variety of reagents were tested in order to elute the adsorbed complex from the column. In order to choose the most effective eluent for the quantitative recovery of copper(II), methylisobutyl ketone, chloroform, acetone, sodium hydroxide, poly-ethylene glycol and ethanol were studied. The adsorption studies were carried out maintaining an overall Cu(II) concentration of 10 µg in 100 mL sample volume. The recovery of copper(II) was found to be quantitative with ethanol and polyethylene glycol as eluting agents. However, polyethylene glycol was preferred owing to its non-inflammability and less toxicity[17,18]. It was observed that when the ratio of polyethylene glycol-water mixture is 7:3, a recovery of 99.7 % could be attained.

Effect of sample volume: The effect of sample volume on the recovery of the analyte was investigated in the range 100-1500 mL maintaining an overall concentration of 0.025 mol L^{-1} sulphuric acid. The resulting complex was eluted using 10 mL of polyethylene glycol. The results are presented in Fig. 2. As can be seen from the figure, it is evident that the recovery of copper(II) is quantitative (> 96 %) up to 1000 mL sample volume. A preconcentration factor of 100 could be attained for quantitative recovery (> 96 %) of Cu(II) when the sample volume was 1000 mL.

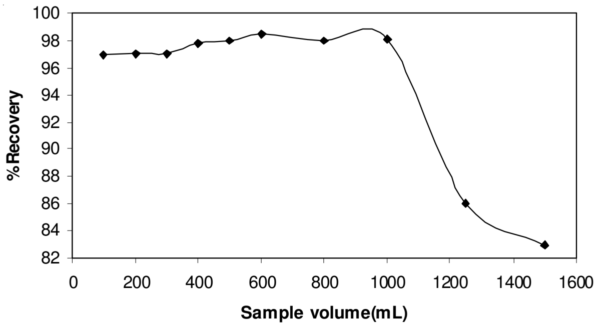


Fig. 2. Effect of sample volume on the recovery of copper

Effect of flow rate: The flow rate of 1-5 mL min^{-1} was found to be suitable for optimum loading of Cu(II) N,N'-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane complex on the neutral C_{18} column. At higher flow rates, there was a reduction in the percentage adsorption of copper(II). This could be probably due to the insufficient contact time between the sample solution and C_{18}. A flow rate of 2 mL min^{-1} was maintained for the elution of copper(II).

Effect of the amount of C_{18}: The amount of C_{18} loaded was varied from 0.25 to 2.0 g and the preconcentration studies were carried as before. Quantitative recovery of Cu(II) could be attained in the range 0.75-2.0 g of C_{18}. For amounts less than 0.75 g there was a significant reduction in the recovery beyond a sample volume of 100 mL.

Precision studies and limit of detection: The precision studies were carried out at 10 μg level of copper(II) by carrying out 10 separate determinations using the above-mentioned procedure. The sample volume was maintained at 100 mL. The relative standard deviation of the method was found to be 3 %. The sensitivity of the developed method is reflected by the limit of detection studies, defined as the lowest concentration of Cu(II) below which quantitative recovery of the metal ion by C_{18} is not perceptibly seen. The limit of detection was found to be 6 μg L^{-1}.

Stability of the column: The stability of the column was tested using 10 μg Cu(II) maintaining a sample volume of 100 mL. The adsorbed Cu(II) N,N'-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane (H_2L_2) complex was eluted using 10 mL of polyethylene glycol-water mixture. The column could be used with good precision and quantitative recovery (> 96 %) for at least 10 cycles. Beyond 10 cycles, there was a significant reduction in the recovery of copper(II).

Effect of other ions: The interfering effect of diverse ions was studied at varying concentrations. The preconcentration studies were carried out as mentioned above using 10 μg Cu(II) maintaining a sample volume of 100 mL. The studies indicated that Na^+, Mg^{2+}, Ca^{2+}, Hg^{2+}, SO_4^{2-}, Cl^-, NO_3^-, Zn^{2+}, Co^{2+}, Fe^{2+} did not cause any significant reduction in the recovery of copper(II). The results (Table-1) are showing the recovery of Cu(II) with varying concentrations of metal ions. The recovery was found to be quantitative in the concentration range of the metal ions that was investigated. Since, the ions that are commonly present in water samples did not interfere significantly, the method was applied to study the recovery of copper(II) in water samples.

TABLE-1
EFFECT OF DIVERSE IONS ON THE RECOVERY OF 10 μg Cu(II) IN A SAMPLE VOLUME OF 100 mL

Recovery of copper (%)	Amount (μg)	Ions
98.5	100	Ca^{2+}
98.6	1000	
97.7	500	
98.7	100	Mg^{2+}
98.8	500	
97.9	1000	
98.5	5	Zn^{2+}
98.4	10	
98.3	25	
98.0	100	Cl^-
98.6	500	
95.4	1000	
98.5	100	NO_3^-
98.4	50	
94.5	1000	
98.0	100	SO_4^{2-}
97.5	500	
96.4	1000	
98.6	5	Co^{2+}
98.5	10	
97.0	25	
96.4	5	Hg^{2+}
95.3	10	
94.7	25	
98.0	100	Fe^{2+}
97.8	250	

Eluent 7:3 PEG-water mixture, flow rate 2 mL min^{-1}.

Recovery studies in tap water and well water samples: The validity of the proposed method was tested by spiking known concentrations of copper(II) to tap water and well water samples. The water samples were filtered and stored in polythene bottles. The recovery of copper(II) was found to be satisfactory with a relative standard deviation of 2 % for five replicate measurements and the results are shown in Table-2.

Analysis of copper(II) content in real sample: To assess the applicability of the method to real samples, it was applied to the extraction and determination of copper(II) from different water samples. Tap water(Tehran, taken after 10 min operation of the tap), rain water (Tehran, 26 January, 2011) samples were analyzed (Table-2).

Comparison with other solid phase adsorbents: The proposed methodology was compared to a variety of solid adsorbents reported recently in the literature. Also, the proposed method was free of interference compared to conventional

TABLE-2
ANALYTICAL RESULTS FOR THE RECOVERY OF Cu(II) IN WATER SAMPLES

Recovery (%)	Sample volume (mL)	Cu(II) found (µg)	Cu(II) added (µg)	Sample
98.4	100	99.7	100	–
97.5	250	99.6	100	Rain
97.6	1000	9.95	10	Water
96.7	100	9.93	10	–
98.7	100	9.92	10	–
98.6	200	9.93	10	Tap
98.5	500	9.92	10	
97.2	750	9.93	10	Water
98.5	1000	9.95	10	–

procedures to determine copper[35,52,53]. As can be seen from the reported works, it is evident that the preconcentration factor obtained with C_{18} is comparable to or even better than most of the other chelating matrices. The other significant feature of the proposed method is the use of environmentally benign polyethylene glycol for the elution of the complex.

Conclusion

The proposed spectrophotometric method for copper(II) is simple, sensitive and exhibits good selectivity. The elution of the complex does not involve strong acids or toxic organic solvents. The advantage of using polyethylene glycol as the eluent lies in the fact that it is non-inflammable, inexpensive and non-toxic. The conventional solvent extraction procedure associated with metal dithizonates is avoided in this methodology. The highest preconcentration factor attainable was 100 for a 1000 mL sample volume. The method showed minimum interferences with commonly found ions in water sample and the recovery of copper(II) was quantitative. The important features of the proposed method are its higher adsorption capacity with good preconcentration factor. The developed method is sensitive in detecting Cu(II) at ppb levels. The column could be used with good precision and quantitative recovery for at least 10 cycles. The quantitative recovery of copper(II) with a low relative standard deviation of 3 % reflects the validity and accuracy of the proposed method when applied to real samples. 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[35,52,53].

ACKNOWLEDGEMENTS

The authors gratefully acknowledged Department of Chemistry, Varamin (Pishva) Branch, Islamic Azad University for financial support.

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