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Sensitized Spectrophotometric Determination of Cu(II) Ion using α-benzoin Oxime in Surfactant Media

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A simple, rapid and selective procedure for spectrophotometric determination of trace amounts of copper in water samples has been described. The method is based on effect of organized molecular assemblies on the spectrophotometric measurement due to their effect on the systems of interest. The ability of micellar system in solubilizing of sparingly soluble ligand or complexes has been used for increasing figures of merit of an analytical method without need to carry out a primary extraction prior to analysis. The spectrophotometric determination of Cu(II) using α-benzoin oxime in the presence of nonionic surfactant Triton-X100 has been performed. The Beers law is obeyed over the concentration range of 0.1-18.6 μg mL^{-1} and detection limit of 2 ng mL^{-1}. The molar absorptivity of complexes is 5754 L mol^{-1} cm^{-1}. The influence of type and amount of surfactant, pH, complexation time, amount of ligand and ionic strength on sensitivity were examined. The effect of common interfering ions on the determination of copper ion was evaluated. The proposed method has been successful with recovery yield of almost 100 % which has been applied to the rapid and simple determination of copper in the real samples.

Key Words: α-Benzoin oxime, Spectrophotometric method, Micelle, Triton-X100, Copper(II).

INTRODUCTION

In many cases, the analysis of heavy metals in environmental samples presents a notable difficulty due to both the low levels of metals in the samples and the high complexity of the matrices[1]. Copper is responsible for gastrointestinal tract irritation but is generally not harmful to humans at low concentration. However, in concentration less than 1 ppm can be toxic to aquatic plants and some fishes[2]. Thus, copper tends to be much more of an environmental hazard than a human hazard. The determination of trace amounts of copper has received considerable attention in many samples especially environmental pollution. Many methods including ICP-MS[3], ion

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chromatography[4], anodic stripping voltammetry[5] and electro-thermal atomic absorption spectrometry[6], extraction and separation methods[7-9] and ion selective electrode[10] have been used for copper determination. Many of these methods are time consuming or require complicated and expensive instruments[11] and some of which use harmful organic solvents. Due to the low concentration of copper content, the development of new sensitive and selective methods for selective, sensitive, rapid and convenient determination of this ion in sub-micron levels is still a challenging requirement.

Organic micellar media are very useful in analytical applications, especially in UV-visible spectrophotometry[12-15] and the fluorescence process[16], because they are stable in aqueous solutions and are transparent optically, enhance sensitivity and are readily available[17]. In surfactant media complexes of metal ions with complexing agents are most stable than those formed in the absence of surfactant due to formation of aggregates that cause an improvement sensitivity and detection limits[18].

For determination of traces of Cu(II) with UV-vis spectrometry, various chelating agents such as sodium diethyldithiocarbamate, cuprizone, and dithizone have been used[19]. Some of them performed with solvent extractions that are time consuming and tedious have lower accuracy and precision and usually involve harmful solvent or need high degree of operator skill or interference of other metals as well.

In order to cope with these difficulties and determine the trace amount of copper using UV-visible spectrometry, recently sensitized spectrophotometric determination of copper ion based on surfactant media have been reported[20-23].

In the present work a simple and highly selective and sensitive spectrophotometric method for the determination of copper(II) ion using α-benzoin oxime (BO) in surfactant media (Trition X-100) has been established. The stability and dissociation constant of complex and α-benzoin oxime were investigated.

EXPERIMENTAL

A Shimadzu UV-vis 160 spectrophotometer was used to measure the absorbance of complex in Triton-X100 media. To adjust the pH and prepare the buffer solution a 691 pH/Ion meter with a combined glass and calomel electrode has been used. The AAS determinations were carried out on a Perkin-Elmer 603 atomic absorption spectrometer with a hallow cathode lamp and a deuterium background corrector, at a wavelength of 324.8 nm (resonance line) using an air-acetylene flame.

All chemicals such as $Cu(NO_3)_2$ and α-benzoin oxime were of the analytical grade purchased from Merck company 0.5 % (w/v). All surfactants, *e.g.*, sodium dodecyl solfonate (SDS), Triton X-100, Brij 58, cetyltrimethyl-ammonium bromide (CTAB), *n*-dodecytrimethylammonium bromide (DTAB) and tetrabuthylammonium perchlorate (TBAP) were prepared by dissolving 0.5 g of surfactant in 100 mL volumetric flask with stirring.

Calibration curve: Standard copper solutions of 100 µg mL^{-1} were prepared and several aliquots of this copper ion solution were added to 10 mL volumetric flask in the range of 0.05-25.0 µg mL^{-1}. To these solutions, 1 mL of 0.001 M α-benzoin oxime and 1.6 mL of 0.042 M Triton X-100 were added and with acetate buffer (pH 4.5) was filled to the mark and calibration curve of copper ion was constructed using a UV-visible spectrometer.

The pH measurement method for speciation of different form of complex was done according to the literature[24]. Two separate solutions were prepared as follows: the first solution contains, 5 mL 0.02735 M α-benzoin oxime, 10 mL 0.5 M KNO_3, 2 mL 0.1 M HCl and 33 mL water; the second solution contain 5 mL 0.02735 M α-benzoin oxime, 5 mL 0.01346 M $CuCl_2$, 10 mL 0.5 M KNO_3, 2 mL HCl and 28 mL water. Both solutions were titrated potentiometrically with 0.0965 M NaOH. From the titration curve of the first solution the acidic dissociation constants of the ligand and from the second titration curve the formation constant of different form of complex were evaluated. According to IUPAC recommendation the detection limit has been calculated[25].

Pretreatment of real samples: The organic content of the waste (Waste of oil refinery, Gachsaran, Iran) samples were oxidized in the presence of 1 % H_2O_2 in a quartz vessel and concentrated nitric acid. The samples were filtered through a filter paper. After acidification to 1 % with concentrated nitric acid, they were stored in polyethylene bottles.

After the pH adjustment of samples to the desired value the spectrophotometric experiment was performed according to the above procedure. A synthetic sample was prepared as Cu^{2+} and 20 fold of Hg^{2+}, Pb^{2+}, Ag^{+}, Zn^{2+} and 10 fold of Ni^{2+} and Co^{2+} and amount of Cu^{2+} ion was found by standard addition method.

RESULTS AND DISCUSSION

In preliminary experiments complexation between Cu^{2+} and α-benzoin oxime was examined using UV-vis spectrophotometry and conductometry and results confirmed a stoichiometric relation copper to α-benzoin oxime equal to 1:2. The complexation between Cu^{2+} and α-benzoin oxime depends strongly on pH. A sensitive and sharp peak at *ca.* 447 nm (where ligand and copper do not show any absorbance) indicate the strong interaction between the Cu^{2+} and the α-benzoin oxime. Using one of the Maple 8 program, speciation of different possible forms of complexes between ligand and Cu^{2+} and evaluating the dissociation constant of ligand and the stability constant of its complexes with Cu^{2+} were examined and are presented in Table-1. The suggested pH range is 4.4-5.8 for the formation of $Cu(BO)_2$ complex. At higher pH, formation of hydroxide inhibited complex formation (Fig. 1).

TABLE-1
LOGARITHM OF CUMULATIVE STABILITY CONSTANTS FOR THE INTERACTION OF H^+ AND Cu^{2+} WITH BO AT 25° C AND IONIC STRENGTH OF 0.1 M

Cu^{2+}	H^+	BO	log β
0	1	1	9.92
0	2	1	16.95
1	0	1	12.17
1	0	2	17.67
1	1	2	26.41

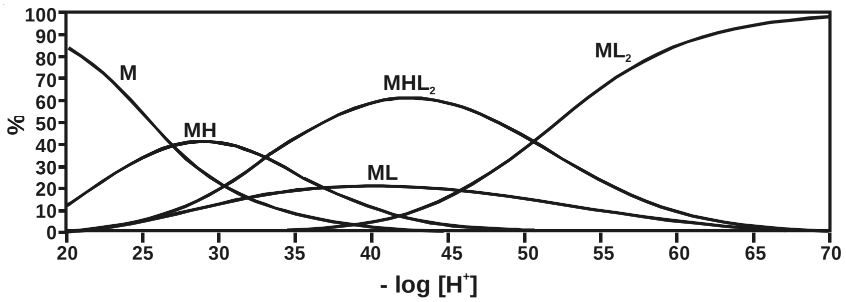

Fig. 1. Speciation of complexes of Cu^{2+} with α-benzoin oxime

The effect of various parameters such as pH, type and amount of surfactant, amount of ligand and ionic strength were examined. Time dependency of complex and effect of interference of other metal ions were evaluated. The method has wide linear range, low detection limit, high sensitivity and selectivity and high repeatability for determination of copper content in real samples.

Absorption spectra of $Cu(BO)_2$ in Triton-X100 media: The ligand, α-benzoin oxime is a N-OH donating ligand base is insoluble in water at neutral pH. Due to the presence of oxime group and incorporation of π electron it acts as a soft acid and bind selectively to soft acid as copper ion in neutral media.

A sensitive and sharp peak (where ligand and copper do not show any absorbance) indicates the strong interaction between the copper and the α-benzoin oxime with molar absorptivity of 5.754×10^3. The absorption spectrum of Cu(II)-α-benzoin oxime was obtained (Fig. 2). Experiment in micellar media has higher sensitivity and does not require the extraction of complex to organic phase. The studies focused on investigation of complexation in micellar media. At optimum pH the time dependency and rate of complex formation were investigated. The results show that the complex was completely formed at 2 min and up to 40 min is stable.

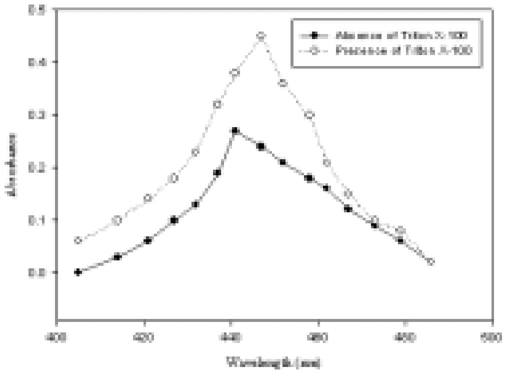

Fig. 2. Comparing Spectra in the presence and absence of surfactant, conditions, α-benzoin oxime (1 mM), pH 4.5, Cu^{2+} (16 µg mL^{-1}) in the presence and absence of Triton X-100 (6.5 mM)

Effect of pH on sensitivity: Due to the presence of oxime group in the ligand structure, the pH has a appreciable effect on sensitivity. The influence of the test solution pH on the absorbance of complex in 6.5 mM Triton-X100 media was investigated and results are summarized in Fig. 3. The complex showed the maximum absorption at pH 4.5. It is assumed that the reaction to form this complex could have competed against hydroxide precipitation at higher pH (basic solution) and ligand protonation at lower pH that lead to reduce in sensitivity, therefore pH 4.5 in acetate buffer has been selected for further studies.

Effect of surfactant on sensitivity: To investigate the effect of types of surfactants, Triton X- 100 and Brij 58 as nonionic, sodium dodecylsulfate as anionic surfactant and cetyltrimethyl ammonium bromide, *n*-dodecyltrimethyl ammonium bromide and tetrabuthylammonium perchlorate as cationic surfactants were examined. In order to asses the effect of type of surfactant, a set of similar experiments at optimum value of other parameters and 6.5 mM of each surfactant has been carried out and results are given in Table-2. It is concluded that in 6.5 mM of Triton X-100 media, the calibration curve with high sensitivity and red shift could be constructed and its slope was about 2 times more than other surfactant.

The observation in presence of non-ionic surfactant, the high sensitivity can be achieved is an indication that surfactant only lead to aggregation of complex and increase in sensitivity. It seems that α-benzoin oxime combines with Cu^{2+} to form a non-polar complex, which is extracted instantaneously into the local non-polar environment of micelle of non-ionic surfactant. Although the concentration of the Triton-X100 were somewhat less than critical micelle concentration (0.0082 M, 0.05 %) and hence

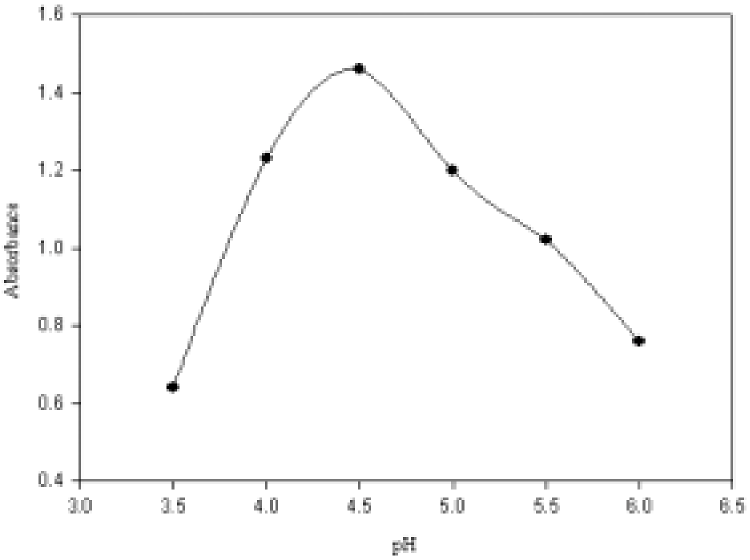

Fig. 3. Effect of pH on sensitivity, conditions, α-benzoin oxime (1 mM), Cu^{2+} (16 µg mL^{-1}), Triton X-100 (6.5 mM)

TABLE-2
EFFECT OF TYPE OF SURFACTANT ON SPECTRA AND SENSITIVITY, CONDITIONS, α-BENZOIN OXIME (1 mM), pH 4.5, Cu^{2+} (16 µg mL^{-1}), DIFFERENT SURFACTANT (6.5 mM)

Surfactant	Absorbance	Maximum Wavelength (nm)
Triton X-100	1.47	447
SDS	1.03	443
CTMAB	0.98	443
Brij 58	1.26	445
DTMAB	1.02	442
TBAP	0.75	430

complex was homogenously dissolved in surfactant media. The 6.5 mM of Triton-X100 has been used for further studies.

Effect of Triton-X100 concentration: Various concentration of Triton X-100 was added to solution at optimum values of other parameters and sensitivity were examined (Fig. 3). The concentration of Triton-X100 surfactant varying from 0.2-8 mM at pH 4.5, the absorbance of desired complex was investigated. The maximum absorbance was obtained at the 6.5 mM concentration of Triton-X100. It is assumed that the concentration of the surfactant was somewhat less than critical micelles concentration complex which was homogeneously dissolved in surfactant media.

Effect of α-benzoin oxime concentration: The analytical sensitivity and the reproducibility in the complex spectra were appreciable in surfactant media. It is known that copper interact stoichiometrically with α-benzoin oxime to form a 1: 2 complex. For evaluating and investigating the effect of the chelating agent concentration various amount of ligand was added to similar solutions at optimum conditions of other variables. Fig. 4 displays that ligand concentration must be exceeding of copper ion concentration to reach high sensitivity. Therefore, α-benzoin oxime was added more than 10 times of copper concentration to reduce fluctuation in measurement of absorbance.

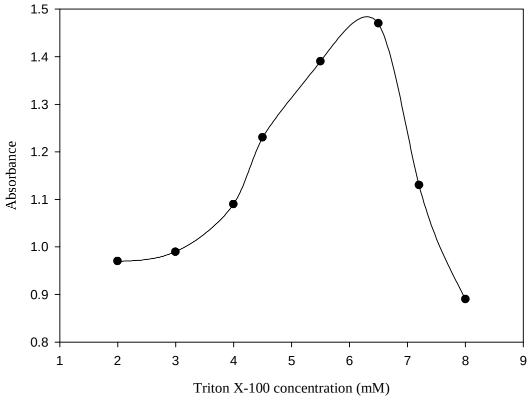

Fig. 4. Effect of Triton X-100 concentration on sensitivity, conditions, α-benzoin oxime (1 mM), pH 4.5, Cu^{2+} (16 µg mL^{-1}), various concentration of Triton X-100

Interference effect: The capability of ligand for complex formation at optimum conditions (Table-3) were investigated by measurement of recover yield (absorbance) in the presence and absence of various amount of common interfering ion that concomitant with copper in real samples. The criterion for evaluating the interference is as following: if the sensitivity in the presence and absence of interfering ion does not differ more that three times of standard deviation of method (reproducibility) the ion does not interfere. Therefore various amount of interfering ion was added to 1 µg mL^{-1} solution of copper and results are shown in Table-4. Results display that method has good selectivity even in the presence of Co^{2+} and Ni^{2+} that this unique selectivity is due to low pH. The selectivity was also examined by considering the concentration of interfering ion in which there is less than 3 % effect on absorbance in the presence and absence of interfering ion which so called tolerance limit.

TABLE-3
TOLERANCE LIMIT OF INTERFERING IONS ON PROPOSED METHOD

Interfering species	Mole ratio of interfering species to Cu(II)
Br^-, SCN^-, Pb^{2+}, Zn^{2+}, Ba^{2+}, Mg^{2+}, K^+, Fe^{2+}	1000
EDTA, Hg^{2+}, Ag^+, Cd^{2+}	600
Ni^{2+}, Co^{2+}	200

TABLE-4
ACCURACY AND PRECISION OF PROPOSED METHODS FOR REAL SAMPLE ANALYSIS

Sample[a]	Added Cu (II)	Proposed Method	RSD (%)	Recovery (%)	Found with AAS
Waste water	0.00	0.769	1.2	----	---
	0.50	1.249	0.9	96.0	1.208 ± 0.003
River Sample	0.00	0.364	1.6	---	---
	1.00	1.341	0.8	97.7	1.350 ± 0.003
Tap water	0.00	B.L.[b]	----	---	---
	1.00	1.023	1.0	102.3	1.036

[a]All values are µg mL^{-1} [b]B. L. below linear range

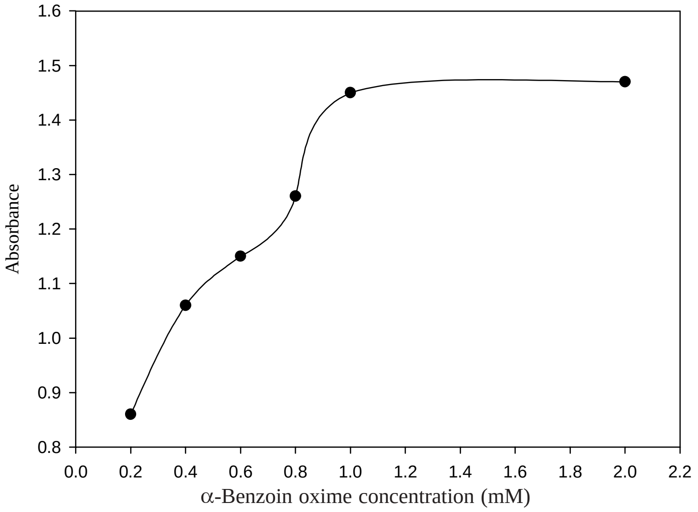

Fig. 5. Effect of α-benzoin oxime concentration on sensitivity, conditions, different amount of α-benzoin oxime, at pH 4.5, Cu^{2+} (16 µg mL^{-1}), Triton X-100 (6.5 mM)

Calibration curve and detection limit: The calibration curve were obtained by using sample solutions at the optimum conditions. A calibration curve was constructed at optimum conditions according to calibration curve procedure in experimental section. The dynamic range of Cu^{2+} was 0.1-18.6 µg mL^{-1} with correlation coefficient (R^2) of 0.9998, showing good linearity of calibration curve. Based on the signals of ten blank solutions and the slope of calibration curve, it was found that the detection limit was 2 ng mL^{-1}.

Analytical application in real samples: The present procedure was tried for the determination of copper ion in different matrices. The procedures were applied to the determination of Cu^{2+} in different samples, including river water, tap water, waste water and synthetic mixture sample. Reliability were checked by spiking experiments and independent analysis. To ensure that the method is valid and has reasonable accuracy and precision, recovery of the Cu^{2+} in the waste water, the tap water and synthetic sample were determined by these proposed techniques and the results are shown in Table-5 has a good agreement with reference AAS method. The low relative standard deviations represent the high reproducibility in these measurements. Therefore, this proposed technique could be applied to the determination of ng mL^{-1} level of Cu^{2+} in real samples.

TABLE-5
FIGURES OF MERIT OF METHOD

Figures of merit	Value
Linear range (μg mL^{-1})	0.1000-18.6000
Regression equation	$0.2534\ C_{Cu}^{2+} + 0.0043$
Correlation coefficient	0.9992
Detection limit[24]	0.0200

Conclusion

The proposed method is advantageous with high reliability, reproducibility, sensitivity, selectivity and high tolerance limit of common ions for rapid and sensitive determination of copper ion in various media. The low RSD of real sample analysis is an indication of methods versatility for real sample analysis. These characteristics and the typical applications presented in this paper, make the methods suitable for measuring the copper content in a wide variety of samples, without a significant interaction from concomitant ionic species.

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