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Highly Selective Catalytic Spectrophotometric Determination of Copper in Water Samples

H. BAGHERI*, M. TABATABAEE, A.A. KERDEGARI, M. SHAHVAZIAN† and M.R. SHISHEHBORE
Department of Chemistry, Islamic Azad University, Yazd Branch, Yazd, Iran
Tel: (98)9121457908, E-mail: h_bagheri82@hotmail.com

A simple, rapid and sensitive method has been developed for determination of trace amounts of copper(II) (1-160 ng mL^{-1}) based on it's catalytic effect on the oxidation of thionine by hydrogen peroxide in an alkaline media and in the presence of *o*-phenanthroline as an activator. The reaction is monitored spectrophotometrically by measuring the decrease in absorbance of thionine at 600 nm by the fixed time method. The detection limit is 0.7 ng mL^{-1} and relative standard deviation for ten replicate determinations of 2, 20, 50 and 100 ng mL^{-1} copper were 1.71, 1.2, 0.98 and 0.75 %, respectively. The proposed method is sensitive, accurate and tolerant to many foreign substances and all the reagents used are stable under the conditions. Moreover, the method is easy to perform for the determination of copper in real samples.

Key Words: Kinetic, Spectrophotometric method, Copper determination, *o*-Phenanthroline, Thionine.

INTRODUCTION

Copper is an important element in industrial and biological systems. Interest in copper found in biological systems is due to the importance of this metal as an essential trace element. Moreover, copper accumulation in liver is a characteristic of Wilson's disease producing neurologic and psychiatric defects. Copper is both vital and toxic for many biological systems depending on its concentration[1,2]. Thus, the determination of trace amounts of copper is becoming increasingly important because of the increased interest in environmental pollution[3].

A number of sensitive analytical methods are available for the determination of copper. Atomic absorption spectrometry[4,5], inductively coupled plasma emission spectrometry[6-8], electrochemical methods[9-11], inductively coupled plasma-mass spectrometry[12,13], fluorometric[14], thermometric[15], spectrophotometric[16-19] and catalytic kinetic methods[20,21] are the most widely used methods. Recently we have reported the determination of trace amounts of copper after preconcentration with 1,5-diphenyl carbazone on microcrystalline naphthalene[22].

The catalytic kinetic methods have shown some very promising features for determination of metal ions in ultra-trace levels. These methods have many advantages such as high sensitivity, good selectivity, required only expediency operation and simple equipments for trace determinations[23].

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†Department of Textile Engineering, Islamic Azad University, Yazd Branch, Yazd, Iran.

Various indicator reactions for the kinetic-catalytic determination of copper have been studied. The poor selectivity or limit of detection, limited linear dynamic range and time consuming of many of existing methods, along with the drawback of requiring a reagent that is not commercially available compared to the proposed method, has necessitated the development of adequate separation procedures.

Copper(II) is a good catalyst for the oxidation of various organic or inorganic reagents in the presence or absence of an activator. In continuation of our research on spectrophotometric determination of some chemical species[24-26], in this paper the application of thionine-H_2O_2 indicator reaction in presence of *o*-phenanthroline as an activator to the catalytic spectrophotometric determination of traces of copper is described. There are a few reports on application of thionine, as an indicator reagent, to the catalytic determination of some species[24,27]. The advantage of this dye is that under the conditions studied, the rate of the uncatalyzed reaction was negligible where the catalyzed reaction showed maximum sensitivity.

EXPERIMENTAL

A Shimadzu Model 160-A UV-Vis spectrophotometer equipped with a quartz cell of 1 cm path length was used for the absorption spectra and the absorbance measurements. A Sartorius pH meter was used for pH adjustments. A thermostat bath was used to keep the reaction temperature at 30 ± 0.1 ºC. A stopwatch was used for recording the reaction time.

All reagents used in this experiment were of analytical grade. Deionized water was used throughout all experiments. Stock solution of 1000 μg mL^{-1} Cu(II) was prepared by dissolving 1.000 g of metallic copper (99.99 %) in conc. nitric acid (1:1). The excess of nitric acid was removed by heating. The mixture was diluted to 1000 mL with water. Working standard solutions were prepared by suitable dilutions of the stock solution. A buffer solution (pH = 10) was prepared by dissolving 6.75 g NH_4Cl and 57 mL of concentrated ammonia solution in water and diluting to 500 mL. A 10 % (v/v) hydrogen peroxide solution was prepared and used. This solution was standardized by iodimetric titration.

A 0.01 M *o*-phenanthroline solution was prepared in a water-methanol (1:1) solution. Thionine reagent (3.48×10^{-4} M) was prepared by dissolving 0.010 g of its powder in 40 mL ethanol and diluting with water to 100 mL. Potassium nitrate solution 2 M was prepared by dissolving its desired amount in water and diluting to 50 mL.

Stock solutions (1000 μg mL^{-1}) of interfering ions were prepared by dissolving suitable salts in water, hydrochloric acid or sodium hydroxide solution.

Recommended procedure: Except the catalyst concentration, which was varied, a set of concentrations of the other reagents was judiciously chosen for analytical procedure after a detailed spectrophotometric kinetic study of the reaction. All the working solutions were thermostated at 30 ± 0.1 ºC for 0.5 h. After thermal equilibrium was established, in a 10 mL volumetric flask, 1.2 mL of buffer solution, 1.4 mL of *o*-phenanthroline 0.01 M, a known volume of copper solution for the catalyzed reaction and then the 0.8 mL of stock thionine solution were placed. The solution was diluted to *ca.* 8 mL with water. Then 0.8 mL of hydrogen peroxide was added to the reaction mixture, followed by dilution to 10 mL with water. Time was measured just after the addition of the hydrogen peroxide solution.

After thorough mixing a portion of this solution was transferred to a cuvette kept in the temperature controlled cell compartment. The progress of the oxidation of thionine by H_2O_2 in alkaline medium was monitored using the fixed time procedure by measuring the change in absorbance at 600 nm for 30-240 s. The absorbance was measured against the blank solution.

The data obtained were used to plot the calibration curves between difference of changes in absorbance after a fixed time (ΔΔA) for catalyzed and uncatalyzed reactions *versus* Cu(II) concentration. This method was followed to avoid the complications, which may arise due to interference by the products or other reagents present in the system. In order to eliminate any traces of metal ions coming from cell surface, we cleaned the cell used in this work scrupulously. Cuvettes were cleaned after use by dipping in nitric acid (1:2) for 15 min to remove traces of species absorbed on the walls.

RESULTS AND DISCUSSION

Under the conditions studied, the thionine solution was negligibly oxidized by hydrogen peroxide (Fig. 1a). Cu(II) at ultra trace levels in presence *o*-phenanthroline can increases the rate of reaction. This oxidation process was monitored by measuring the decrease in absorbance with time at 600 nm (Fig. 1b).

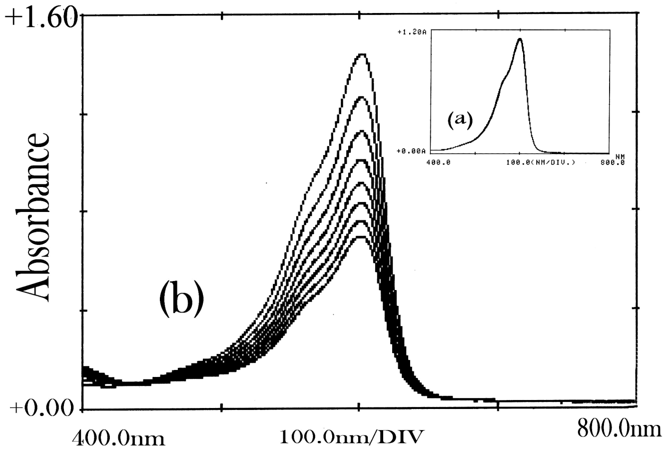

Fig. 1. Absorption spectra of reaction system. Conditions: Buffer pH=10; *o*-phenanthroline, 1.4×10^{-3}; thionine, 2.78×10^{-5} M; 0.8 mL H_2O_2 10 % (v/v) and temperature 30 °C with scan time intervals of 30 s to 240 s: in the absence of copper(II) (a) and in the presence of copper(II) (b)

Optimization of reaction variables: The reaction variables were optimized in order to maximize the sensitivity and precision of the proposed catalytic kinetic method. The effects of pH, reagent concentrations, ionic strength, temperature and time on the reaction were studied. Where each variable was changed in turn keeping all other constant. The optimum conditions used for the final working procedure in order to obtain best figures of merit.

Effect of pH: The effect of pH on the catalyzed and uncatalyzed reaction in order to determination of copper was investigated spectrophotometrically. For this purpose, the solution was measured in the pH range of 6 to 12 for pH adjustment. The results obtained are shown in Fig. 2. As it was clearly seen, the sensitivity was the highest at pH = 10.

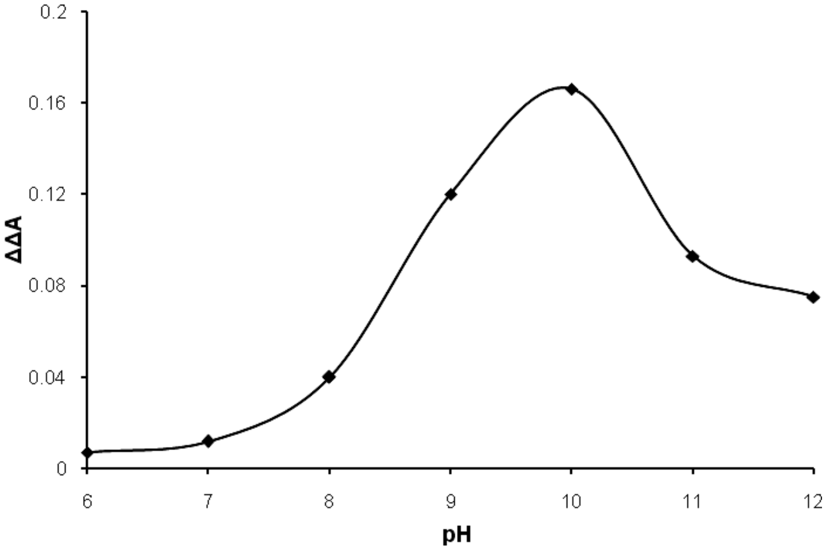

Fig. 2. Effect of buffer pH; Conditions: *o*-phenanthroline, Cu(II), 20 ng mL^{-1}; 1 × 10^{-3}; Thionine, 2.44 × 10^{-5} M; 1 mL H_2O_2 10 % (v/v) and temperature 30 ºC

The variation effect of basicity on the oxidation rate of 2.44 × 10^{-5} M thionine in presence of 1.0 × 10^{-3} M *o*-phenanthroline, 20 ng mL^{-1} copper and 1 mL H_2O_2 10 % (v/v) was studied. As the buffer volume (from 1 to 2.5 mL) had no effect on the difference between the absorbance changes of the catalyzed and uncatalyzed reaction, 1.2 mL ammoniacal buffer with pH = 10 was used in subsequent experiments.

Effect of reagent concentrations: The effect of *o*-phenanthroline on the catalyzed and uncatalyzed reactions rate was monitored in range of 2 × 10^{-4} to 1.8 × 10^{-3} M. The results show the catalyzed reaction rate in presence of *o*-phenanthroline increased and optimum concentration was 1.4 × 10^{-3} M (Fig. 3). Higher concentrations of *o*-phenanthroline caused a negligible decrease in the rate of the reaction.

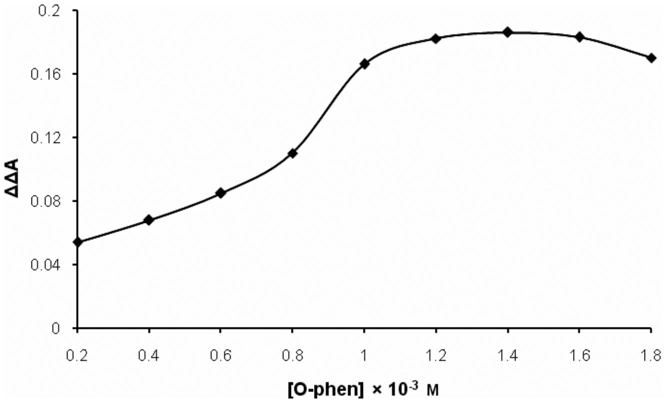

Fig. 3. Effect of *o*-phenanthroline concentration. Conditions: buffer pH = 10, Cu(II), 20 ng mL^{-1}; thionine, 2.44 × 10^{-5} M; 1 mL H_2O_2 10 % (v/v) and temperature 30 °C

The influence of the concentration of thionine on the reactions was studied in the range of 6.96 × 10^{-6} to 2.78 × 10^{-5} M under the optimum pH and concentration of *o*-phenanthroline. Results show that the rate of catalyzed reaction increases linearly with increasing thionine concentration, but the uncatalyzed reaction shows a lower increase. A limited range owing to the high molar absorptivity of the dye should be used that provides an absorbance in the range of minimum photometric error. Therefore, 2.78 × 10^{-5} M was chosen as the optimum concentration (Fig. 4).

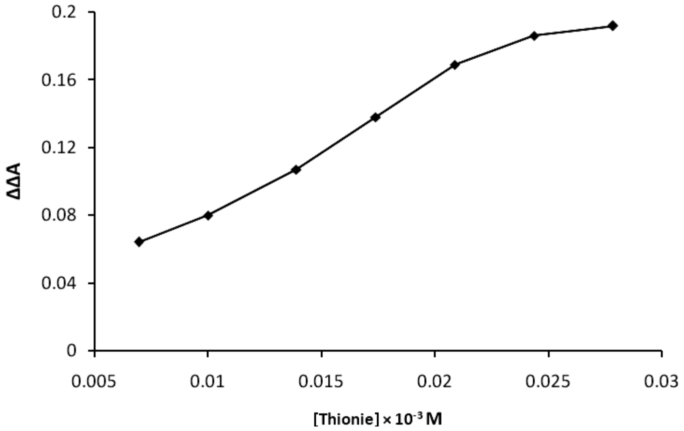

Fig. 4. Effect of thionine concentration. Conditions: buffer pH = 10; *o*-phenanthroline, 1.4 × 10^{-3}; Cu(II), 20 ng mL^{-1}; 1 mL H_2O_2 10 % (v/v) and temperature 30 ºC

The effect of oxidizing agent on the catalyzed and uncatalyzed reaction rate was investigated under optimum pH, *o*-phenanthroline and thionine concentration in the range 0.1 to 1.2 mL of hydrogen peroxide 10 %. According to experiment, the catalyzed reaction rate increases more than that of the blank at hydrogen peroxide volume of 0.8 mL. Thus, 0.8 mL of H_2O_2 10 % (v/v) was used in the experiments.

Effects of ionic strength, temperature and time: The effect of ionic strength on the reaction rate was investigated, the ionic strength being varied from 0.02 to 0.3 M using 2 M potassium nitrate solution. According to the results, this parameter had no effect on the reaction rate.

The influence of temperature on the reaction rate was studied in the range of 15-65 ºC in the optimum conditions. Both reaction rates increased with increasing temperature. It shows that, there is the best sensitivity at 30 ± 0.1 ºC. Finally, the reaction rate was studied in the range of 30-600 s in the presence of optimum conditions. It was found that the maximum changes in absorbance occurs 240 s after the initiation of the reaction and 4.0 min was selected.

Analytical parameters: A calibration graph for determination of copper was prepared under optimum experimental conditions with the fixed-time method. Measurements were for 240 s from initiation of the reaction; because it provided the best regression and sensitivity and reaction time. Beer's law is obeyed within a wide range of 1-160 ng mL^{-1} of copper at 600 nm with a correlation coefficient (r) of 0.9987. The regression equation was $\Delta\Delta A = 8.8 \times 10^{-3}$ [Cu(II)] + 3.6×10^{-3}. The relative standard deviation for ten replicate determinations of 2, 20, 50 and 100 ng mL^{-1} copper were 1.71, 1.2, 0.98 and 0.75 %, respectively. Compared with other methods mentioned in previous section, the sensitivity of this proposed method was very high.

Effect of diverse ions: The effect of potential diverse ions on the determination of Cu(II) ion at optimum conditions were investigated by addition known concentrations of each ion to a fix Cu(II) ion concentration and measurement of the absorbance in the presence and absence of various amount of common interfering ion that concomitant with copper in real samples.

If the sensitivity and recovery efficiency in the presence and absence of interfering ion does not differ more than 3 % signal analyte signal in absence of the interfering ion, does not interfere. Therefore various amount of interfering ion was added to 60 ng mL^{-1} of Cu(II) ion and results are shown in Table-1. The method has good selectivity even in presence of cobalt and nickel ion.

TABLE-1
EFFECT OF FOREIGN IONS ON THE DETERMINATION OF COPPER(II)

Species	Tolerance ratio ions to Cu^{2+} (w/w)
Ba^{2+}, Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, CO_3^{2-}, Cl^{-}	> 5000
SCN^{-}, NO_3^{-}, SO_4^{2-}, HPO_4^{-}, Br^{-}, CN^{-}, NH_4^{+}, Mo^{6+}, Cr^{6+}, Cr^{3+}, Se^{4+}, $C_2O_4^{2-}$, Ag^{+}, Fe^{3+}	> 1000
Mn^{2+}, Fe^{2+}	> 500
ClO_4^{-}, $S_2O_3^{2-}$, Ni^{2+}, Zn^{2+}, Cd^{2+}, SO_3^{2-}	> 200
Co^{2+}	> 80

Application: To evaluate the analytical applicability of the method, the recommended procedure was applied to the determination of copper(II) in river water, spring water, tap water, sea water and boiler water using standard addition method.

Results are described in Table-2. The proposed method was applied and achieved recoveries varied from 99 to 102 %. The used method had a good accuracy. As seen, the results of ten analyses of each sample obtained by the proposed method and atomic absorption spectrometry (AAS) are in satisfactory agreement. It proved that the method can be used for copper determination in water samples.

TABLE-2
COPPER DETERMINATION OF REAL SAMPLES

Samples	AAS method (ng mL^{-1})	Proposed method			Recovery (%)	RSD (%) (n = 10)
		Detected (ng mL^{-1})	Added (ng mL^{-1})	Found (ng mL^{-1})		
River water	104.0	106.0	20	125.8	99.0	0.66
Spring water	39.0	37.0	20	57.3	101.5	1.06
Tap water	28.5	30.0	10	40.1	101.0	0.71
Sea water	38.2	36.7	10	46.9	102.0	0.87
Boiler water	–	–	25	25.0	100.0	1.18

Conclusion

This new method offers several distinct advantages such as high selectivity and sensitivity, ease of operation and rapidity, cheaper reagents are necessary and the instruments are simple and need only minimum maintenance for the determination of Cu(II) without the need for extraction, preconcentration and pre-separation. It offers advantages like reliability and reproducibility in addition to its simplicity and suffers from less interference. It has been successfully applied to the determination of copper at trace level real samples with satisfactory results.

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