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Catalytic Kinetic Spectrophotometry Determination of Trace Copper(II) by H₂O₂ Oxide Acid Fuchsin

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In this work, kinetic spectrophotometric method for the determination of trace amounts of Cu(II) in the range of 4.0-24 ng mL^{-1} is reported. The method is based on the catalytic effect of Cu(II) on the oxidation reaction of acid fuchsin by hydrogen peroxide in presence of dilute sulphuric acid (pH = 2.5). The reaction is followed by spectrophotometrically by measuring the change in absorbance (ΔA) at 546 nm using a fixed time method (6 min). The reaction variables were optimized in order to achieve the highest sensitivity. The 3 s criterion detection limit was 1.36 ng mL^{-1} and the method was successfully applied to the determination of copper(II) in Songhua-river of Heilongjiang province in China.

Key Words: Copper(II), Acid fuchsin, Catalytic kinetic spectrophotometry.

INTRODUCTION

The copper, an essential trace element, which is present in a wide variety of plants[1], animals[2] and natural environment[3], found in the human body and important in metabolism. As a consequence of rapid industrialization, the increase in copper concentrations in the environment results from industrial and domestic waste discharge, disposal of mining washings, refineries and the use of copper as a base material for anti-fouling paint[4]. Copper is essential to human health, but only in limited amounts. Hereditary diseases such as Wilson's disease retain excessive amounts of copper in the body and cause fatal consequences like liver damage[5]. Therefore, determination of trace amount of copper(II) ion in natural water has attracted increasing attention.

Kinetic-spectrophotometric methods have been recognized as offering a valuable approach to trace analysis[6]. The advantage of the catalytic kinetic method lies in the fact that the only instrumentation required is a spectrophotometer. There have been applied in many methods for the catalytic determination of copper(II) based on various redox reactions with photometric detection[7-10]. The addition of a clean catalyst as an activator to catalyzed reactions can also improve the sensitivity of these methods[11,12]. In the present paper, we wish to report a new indicator system for the sensitive, selective and reproducible kinetic spectrophotometric determination of trace amounts of copper. The method is based on the oxidation reaction of acid fuchsin by the H₂O₂ in presence of dilute sulphuric solution medium.

EXPERIMENTAL

Absorption spectra was recorded on a Model 2401 UV-visible spectrophotometer with a 1 cm glass cell and all absorption measurements were taken using a Model 722 visible spectrophotometer (spectrum instrument Co. Ltd. in Shanghai). DK-98-1 electricity heat constant temperature water bath (Taisite instrument Co. Ltd. in Tianjin), A Metrohm Model 632 pH meter with a combined glass electrode was used for pH measurements.

All reagents were of the highest purity available and used without purification. Distilled deionized water was used throughout. Stock solution of 1 g mL^{-1} [Cu(II)] was prepared by dissolving 0.3934 g of CuSO₄·5H₂O in 100 mL of water in a volumetric flask. The acid fuchsin solution(1.76×10^{-4} mol L^{-1}) was prepared by dissolving 0.1028 g of acid fuchsin in 1000 mL of water. 0.018 mol L^{-1} H₂SO₄ was prepared by dilution concentrated sulphuric acid in the volumetric flask.

The catalyzed reaction was monitored spectrophotometrically by measuring the change in absorbance at 546 nm. Placed appropriate amount of standard solution of copper and blank in reaction test tubes. Then added 4 mL solution of acid fuchsin, 1.5 mL H₂SO₄ and 2 mL H₂O₂ volume of solution was diluted up to 25 mL with double distilled water. After mixing, the reaction was carried out in a boiling water bath (100 ℃). In the meantime, a stop watch was opened. After 6 min reaction in boiling water, took out test tubes and immediately placed in cold water to stop the catalytic reaction. After cooling to room temperature, a portion of this solution was

transferred to a glass cell and the absorbance was measured after the initiation of the reaction. A blank solution was also prepared in the same way without the addition of Cu(II).

RESULTS AND DISCUSSION

Effect of pH: Determination of various wavelengths showed that the maximum blank absorbance was 546 nm. At different pH the ΔA was different. The dependence of the rate on pH was investigated in the pH range of 1-6, which is available conveniently with the dilute sulphuric solution. A series of solutions containing 4 mL acid fuchsin, 2 mL H_2O_2, 1 mL standard solution Cu(II) and different concentrations of H_2SO_4 were determined with the oxidization method. A linear dependence of ΔA on pH was observed in Fig. 1. ΔA was the maximum at pH 2.5. The result shows that while pH increases from 1 to 6, the ΔA increases firstly and decreases afterwards. It reaches its maximum when pH is about 2.5. The decolourization reaction of acid fuchsin cannot be efficiently catalyzed by copper(II) in the middle medium, while copper(II) produces a strong catalytic reaction in the acid medium. Therefore, pH = 2.5 was chosen as the optimum working pH.
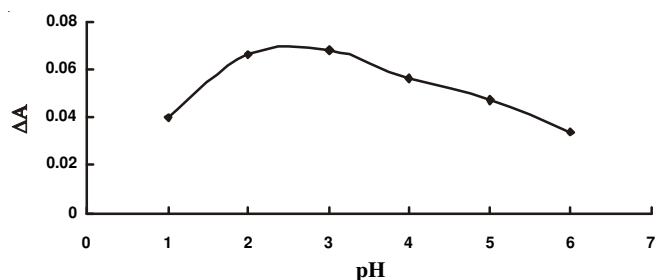

Fig. 1. pH effect

Volume of hydrogen peroxide: Table-1 shows that ΔA increased with increasing hydrogen peroxide. When the volume of H_2O_2 was 2 mL, ΔA was the best. The volume of H_2O_2 increased beyond 2 mL, ΔA decreased more quickly. Therefore, 2 mL H_2O_2 was chosen for further study.

TABLE-1
DIFFERENT H_2O_2 CONTENT TO THE VALUE OF A_0, A AND ΔA

$V_{H_2O_2}$ (mL)	A	A_0	(A_0-A)
0.50	0.305	0.337	0.032
1.00	0.293	0.360	0.067
1.50	0.215	0.285	0.070
2.00	0.184	0.255	0.071
2.50	0.164	0.232	0.068
3.00	0.145	0.212	0.067

Influence of temperature: The influence of temperature on catalyzed reaction was studied between 60 and 100 ºC and was remarkable. The reaction rate was found to increase with increasing temperature. The rate of disappearance of copper(II) followed a first order rate law. The values of first order rate constants at the different temperature are given in Table-2. As the reaction proceeds well within a measurable rate at 100 ºC, so a temperature 100 ºC was selected for further study.

Work curve and detection limit: The calibration graph was prepared by using the recommended procedure under the

optimum conditions. The catalytic reaction rate increased with increasing temperature. In boiling water (100 ºC), when the reaction was carried out for 6 min (Fig. 2), a linear calibration graph was obtained in the range of 4-24 ng mL^{-1} and the equation of $\Delta A = 0.00261c + 0.02307$ was found, where c is the concentration of Cu(II) in ng mL^{-1}. The correlation coefficient of the graph was 0.9898. The relative standard deviation of ten replicated determinations of 1 µg mL^{-1} of copper(II) (n = 10) was 0.95 %.

TABLE-2
ΔA VALUE OF DIFFERENT TEMPERATURE

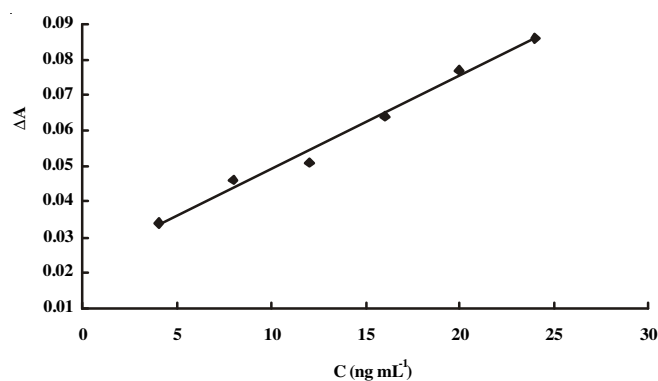| T (ºC)	A	A_0	(A_0-A)
60.0	0.498	0.500	0.002
70.0	0.444	0.476	0.032
80.0	0.376	0.419	0.043
90.0	0.309	0.359	0.050
100.0	0.193	0.265	0.072

Fig. 2. Work curve

The limit of detection (LOD) was evaluated according to the IUPAC method using equation $LOD = KS_b/m$ (K = 3, S_b is the standard deviation of the blank and m is the slope of the calibration graph) was 1.36 ng mL^{-1}.

Kinetics of the indicator reaction and optimization: The detailed mechanistic anatomy of any indicator reaction is a necessary pre-requisite for its exploitation to the analytical application by the kinetic method. Therefore, the kinetics of the oxidation of acid fuchsin by H_2O_2 were investigated under various conditions. Preliminary experiments were performed to determine the suitable conditions of temperature and concentrations of the reactants. Based on the experiment, the optimal reagent imputing quantity is a solution system composed of 4 mL liquor of acid fuchsin, 2 mL liquor of 20 % H_2O_2 and 1.5 mL liquor of diluted sulphuric acid, heating over 6 min in boiling water. The measuring results were the high accuracy and precision and low detection limit.

Interference effects: The interference effects of the presence of different cations and anions on the kinetic determination of copper(II) ($C_{Cu(II)}$ = 16 ng mL^{-1}) were examined and the tolerance limits for interfering ions are summarized in Table-3. A relative error of 5 % was considered tolerable.

Application: Pipette 0.8 mL Songhua River's water, add 4 mL acid fuchsin, 2 mL liquor of 20 % H_2O_2 and 1.5 mL diluted sulphuric acid in sequence, heating over 6 min in boiling water. The absorbance (A and A_0) were measured by ultraviolet spectrophotometer and the content of Cu(II) was calculated

according to A value. The results obtained by the proposed method are given in Table-4. The method has also been applied to the determination of trace copper in Songhua River's water samples with the relative standard deviation of 0.307-2.05 % and the recovery of 98.5-107.3 %. In the present method, the time required for the analysis is only 6 min without the use of any costly solvent, other chemicals and sophisticated instrumentation.

TABLE-3
TOLERANCE LIMIT OF FOREIGN IONS ON THE DETERMINATION OF 16 ng mL^{-1} OF Cu(II)

Interfering ions	Tolerance ratio of foreign ions to Cu(II)
Mg^{2+}, Ba^{2+}, K^+, Na^+	1000
NO_3^-, SO_4^{2-}, SCN^-, Cl^-, ClO_4^-	500
Al^{3+}, NO_2^-, BrO_3^-, Sr^{2+}	100
NH_4^+, F^-, I^-, $S_2O_3^{2-}$, Zn^{2+}	50
Fe^{3+}, Co^{2+}, Ni^{2+}	30
Sn^{2+}, Cr^{3+}, Cd^{2+}	10

TABLE-4
DETERMINATION RESULTS OF Cu(II) IN SAMPLES OF SONGHUA RIVER

	1	2	3	4
ΔA	0.038	0.039	0.037	0.039
m_{Cu} (µg)	0.285	0.304	0.266	0.304
Average content (µg)	0.290			
Standard added amount (µg)	0.200	0.300	0.400	0.500
Average value (µg)	0.488	0.596	0.719	0.770
Recovery (%)	101.0	101.9	107.3	96.0
RSD (%)	0.648	2.05	0.307	0.927

Conclusion

A simple and sensitive method with good selectivity is proposed for the determination of copper in the range of 4.0-24 ng mL^{-1} using the catalytic effect of copper and activating effect of hydrogen peroxide on acid fuchsin reaction. The proposed method can be applied to the analysis of copper in Songhua river's water samples with good precision and accuracy. This method is simple, easy and economical in comparison to the other sophisticated method available in literature.

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