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Kinetic Spectrophotometic Determination of Trace Amounts of Copper Based on its Catalytic Effect on the Reaction of DBC-Arsenazo and Hydrogen Peroxide

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A new catalytic-kinetic spectrophotometric method is proposed for the determination of copper, based on the catalytic effect of copper(II) on the oxidation of dibromo-*p*-chloro-arsenazo (DBC-ASA) by hydrogen peroxide in the acid medium of 1.2×10^{-3} mol/L H_3PO_4. The copper can be determined spectrophotometrically by measuring the decrease in the absorbance of DBC-arsenazo at the wavelength of 514 nm using the fix-time method. The optimum reaction conditions are as follows: 1.2×10^{-3} mol/L of H_3PO_4 of medium, 4.0×10^{-5} mol/L of DBC-arsenazo, 0.18 mol/L of H_2O_2, reaction temperature 100 ºC and reaction time 8 min. The linear range of the method for the determination of copper(II) is between 0.1-1.2 µg in 25 mL of solution and the limit of detection is 3.2 ng/mL. The method has been successfully applied to the determination of copper in water samples.

Key Words: Copper(II), Catalytic-kinetic spectrophotometry, DBC-Arsenazo, Hydrogen peroxide, Water sample.

INTRODUCTION

Copper is one of indispensable special micro-amount elements for the health of human body. The copper content in the body of an adult is about between 1.4-2.1 mg in per kilogramme avoirdupois. An inner of the body of a 60 kg health person should contain about 0.1 g of copper. Although this amount is small, it is extremely important and indispensable for maintaining the health of a human body. Mankind and plants can absorb copper *via* water source. Thus, the determination of copper in water body has a very important significance.

Although some methods have been used in the determination of copper including atomic absorption spectrometry[1], ICP -AES (inductively coupled plasma-atomic emission spectrometry) method[2], liquid phase chromatography methods[3], these methods have the disadvantages that the instrumentation is expensive,operation is

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complex, *etc*. Besides these methods, the studies of some new methods are in progress. Catalytic kinetic spectrophotometry is one among them[4]. Catalytic kinetic photometric analysis has the advantages that the equipment is simple, sensitivity is high and operation is simple. There are the report on the catalytic kinetic photometric methods for the determination of trace copper in recent years[5-9], development of a new system for the determination has still an important significance due to poor selectivity of most reported methods. DBC-Arsenazo (dibromo-*p*-chloro-arsenazo) [IUPAC name: 3-(2,6-dibromo-4-chlorophenylazo)-6-(2-arseno-phenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid ($C_{22}H_{14}N_4O_{11}S_2Br_2ClAs$], Fig. 1), is an unsymmetric *bis*-arylazo derivatives of chromotropic acid that has been used for the spectrophotometric determination of rare earths[10].

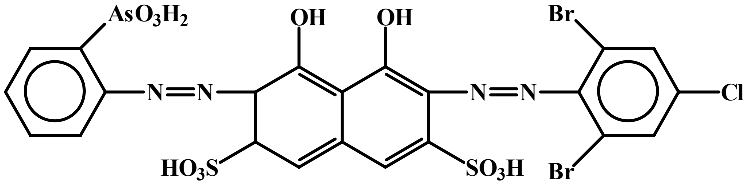


Fig. 1. Molecular structure of DBC-ASA

The aromatic ring in DBC-arsenazo carries -OH, $-SO_3H$, $-AsO_3H_2$, -N=N-, the ligands containing multi-N,O, respectively. The reagent not only has a strong complex ability and forms various water-soluble complexes with metal ions, but also the -N=N- group itself can produce colour. When it is oxidized or reduced, the -N=N- group is destroyed, resulting in the colour of solution to become shallow even achromaticity. It is found in this studies that in the medium of 1.2×10^{-3} mol/L H_3PO_4, copper(II) catalyzes the decolouring reaction of DBC-arsenazo oxidized by H_2O_2 and based on this principle a new method for the determination of trace copper was developed. The present procedure was applied to the determination of copper in water samples with satisfactory results.

EXPERIMENTAL

A 722S spectrophotometer (Shanghai Lingguang Technique Co., Ltd., China) equipped with 1 cm quartz or glass cells was used for all absorbance measurements. A HH-2 digital display constant temperature water-bath boiler (Jintan City Ronghua Instrumental Manufacture Co. Ltd., China) was used for the control of temperature. A stop watch was used for recording the reaction time.

Cu(II) standard solution: 0.3929 g of $CuSO_4 \cdot 5H_2O$ was dissolved in the water acidified by 0.10 mL of concentrated H_2SO_4, then the solution was diluted with water to 100 mL. A 1.000 mg/mL of stock solution was obtained. When it is needed for use, the stock solution was gradually diluted with water to 0.5 μg/mL of working solution. DBC-Arsenazo solution: 1.0×10^{-3} mol/L. 0.0844 g of DBC-arsenazo was dissolved in a definite amount of water and diluted to 100 mL with water. H_3PO_4 solution: 0.030 mol/L. 1 mL of 15 mol/L H_3PO_4 solution was diluted to 100 mL and 0.15 mol/L H_3PO_4 solution was obtained. From the solution 20 mL was taken out and diluted with water to 100 mL, 0.030 mol/L H_3PO_4 solution was obtained. H_2O_2 solution: 1.5 mol/L. 8.4 mL of 30 % (v/v) H_2O_2 solution was taken out and diluted to 50 mL. 1.5 mol/L H_2O_2 solution was obtained. Unless specially stated, all reagents were of analytical grade. The water used in the experiments was quadratic deionized water.

Recommended procedure for copper: In a 25 mL comparison tube, 1.0 mL of a 1.0×10^{-3} mol/L DBC-arsenazo solution was added, followed by the addition of 1.0 mL of 0.030 mol/L H_3PO_4 solution, an appropriate amount of copper(II) standard solution (For conditional experiments, 1.0 µg) and 3.0 mL of 1.5 mol/L H_2O_2 solution. The mixture was diluted to the mark with water and shaken up. Then, it was kept in a water-bath boiler maintained at 100 °C for 8 min. The contents were rapidly taken out and cooled by running water for 5 min to terminate the reaction. The absorbance was measured in 1 cm cells at 514 nm against water. The measurements were taken in the absence or presence of copper(II) against water, which belonged to a non-catalytic (A_0) or catalytic (A) reaction, respectively. Then, the difference in the absorbance between a non-catalytic and catalytic reaction was calculated.

Procedure for the determination of copper in tap water: 10.00 mL of tap water was accurately taken out, placed in a 25 mL comparison tube, then determined for copper content according to the standard procedure. Meanwhile, the experiments of addition standard recovery were made and the results of atomic absorption spectrometry were used as contrast results.

Procedure for the determination of copper in lake water: 1.000 L of lake water was accurately taken out and heated for concentration to about 50 mL. 3.0 mL of aqua regia (1:1, v/v) was added to the content. The contents were heated to near dryness and cooled. Then, in turn 3.0 mL of 1:1 (v/v) hydrogen chloride solution and 3.0 mL of 30 % (v/v) hydrogen peroxide was added. The solution was evaporated to near dryness. After cooling, the content was dissolved in an appropriate amount of water, transferred to a 25 mL volumetric flask and diluted to the constant volume. 1.00 mL of the sample was accurately taken out and placed in a 25 mL comparison tube. The remainder was the same as the standard procedure for the determination of copper. Meanwhile, the experiments of addition standard recovery were made and the results of atomic absorption spectrometry were used as contrast results.

RESULTS AND DISCUSSION

Absorption spectra: According to the standard procedure the absorption spectra of catalytic reaction and non-catalytic reaction solutions were determined (Fig. 2). It can be found form the figure by comparison between curve A of DBC-ASA solution against water and curve B of (DBC-ASA)-H_2O_2 against water that after the addition of hydrogen peroxide to DBC-ASA solution, the absorbance (curve B) decreased to some extent, but this change is not large. This suggested that DBC-ASA can be oxidized by hydrogen peroxide but the oxidation speed is not large and the sensitivity of the reaction is small. After the addition of copper(II) to (DBC-ASA)-H_2O_2 system, absorbance (curve C) obviously decreased. This showed that copper(II) has a catalytic effect on the oxidation of DBC-ASA by H_2O_2. The maximum absorption wavelengths of the catalytic reaction and non-catalytic systems are both at 514 nm. At this wavelength the difference of absorbance was a maximum (curve D). Thus, 514 nm was selected as determination wavelength.

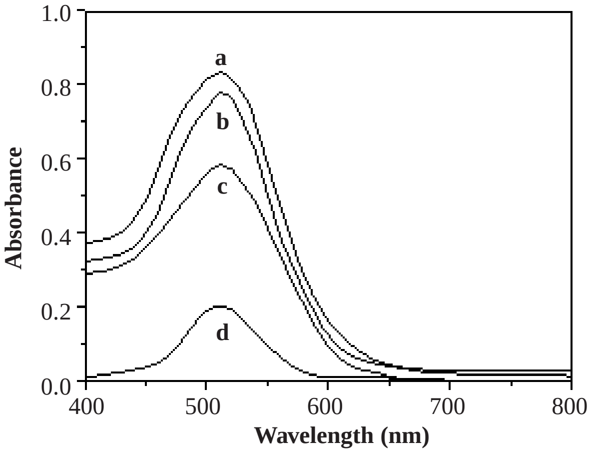


Fig. 2. Absorption spectra: (a) DBC-ASA (against water); (b) (DBC-ASA)-H_2O_2 (against water), A_0; (c) Cu(II)-(DBC-ASA)-H_2O_2 (against water), A; (d) $\Delta A = A_0 - A$: Cu(II)-(DBC-ASA)-H_2O_2 (against reagent blank); $[Cu^{2+}] = 6.3 \times 10^{-7}$ mol/L; [DBC-ASA] $= 4.0 \times 10^{-5}$ mol/L; $[H_2O_2] = 0.18$ mol/L; $[H_3PO_4] = 1.2 \times 10^{-3}$ mol/L; heat temperature T = 100 ºC; heat time t = 8 min

Optimization of reaction conditions

Effect of reaction acidity: Under the condition that other experimental variables were kept optimum, the experiments of acidity effect were made. 0, 0.5, 0.8, 1.0, 1.2, 1.5 and 2.0 mL of 0.030 mol/L H_2PO_4 solution was added, respectively. The results showed that the sensitivity increased with increasing the amount of H_3PO_4 over the range 0-1.0 mL. When the amount of H_3PO_4 was at 1.0 mL, ΔA was maximum and the reaction sensitivity was the highest. Further increase in the amount of H_3PO_4 led to decrease in reaction sensitivity. Therefore, 1.0 mLof 0.030 mol/L H_3PO_4 solution was chosen. At this time, the concentration of H_3PO_4 was 1.2×10^{-3} mol/L.

Effect of the amount of DBC-arsenazo: Under the condition that other experimental variables were kept optimum, the experiments of the effect of the amount of DBC-ASA were carried through. 0, 0.2, 0.5, 0.8, 1.0, 1.1, 1.3, 1.5, 2.0, 2.5 and 3.0 mL of 1.0 × 10^{-3} mol/L DBC-ASA solution was added, respectively. The results showed that as the amount of DBC-ASA increased over the range 0-0.8 mL, ΔA increased. When the amount of DBC-ASA was 0.8-1.1 mL, ΔA was maximum. After it, ΔA still increased with increasing the amount of DBC-ASA In order to keep a suitable sensitivity and consider the effect of amount of the chromogenic agent on the linear range of a calibration curve, 1.0 mL of 1.0 × 10^{-3} mol/L DBC-ASA solution was selected to be the appropriate amount.

Effect of the amount of H_2O_2: Under the condition that other experimental variables were kept optimum, the experiments of the effect of the amount of H_2O_2 were carried through. 0, 1.0, 2.0, 2.5, 3.0, 3.5 and 4.0 mL of 1.5 mol/L H_2O_2 solutions were added, respectively and contrasted with blank reagent. The results showed that with increasing in the amount of H_2O_2 the sensitivity of the catalytic reaction increased over the range 0-3.0 mL. When the volume of H_2O_2 solution was 3.0 mL, the reaction sensitivity was maximum. When the volume of H_2O_2 solution was more than 3.0 mL, the reaction sensitivity decreased. Thus, 3.0 mL of 1.5 mol/L H_2O_2 solution was chosen.

Effect of the amount of reaction temperature: Under the condition that other variables were kept optimum, the experiments of the effect of reaction temperature were carried through. A water bath of 60, 70, 75, 80, 85, 90, 95 and 100 ºC was employed for heat, respectively. The results showed that under the test condition below 60 ºC catalytic reaction can not carry through. As reaction temperature increased, the sensitivity of reaction increased. When the temperature of water bath reached 100 ºC, ΔA was maximum and the reaction sensitivity was the highest. Therefore, the water bath of 100 ºC was employed for heat and the reaction was terminated by running water. The data obtained over 75-100 ºC was regressed and disposed to obtain a linear regression equation: $\log \Delta A = 0.6813-144.08/T$, with a correlation coefficient $r = 0.9923$. The apparent activation energy of the catalytic reaction was calculated to be $Ea = 27.60$ kJ/mol.

Effect of heat time: Under the condition that other experimental variables were kept optimum, the experiments of the effect of heat time were put up. A heat time of 0, 1, 3, 5, 7, 8, 9, 10 and 12 min was employed, respectively. Under the reaction conditions, the absorbance difference is a linear function of time over the range of 1-8 min and at 8 min ΔA was a maximum. The linear regression equation between the absorbance difference and heating time is as follows: $\Delta A = 0.0193t$ (min) + 0.0032, $\gamma = 0.9990$, where t is heat time and γ is the correlation coefficient, respectively. In the experiments heat time was chosen as 8 min and cool time was selected as 5 min by running water to terminate the reactions. The rate constant of the reaction was calculated to be $k = 1.93 \times 10^{-4}\ s^{-1}$. The half-life period was 3.56 min.

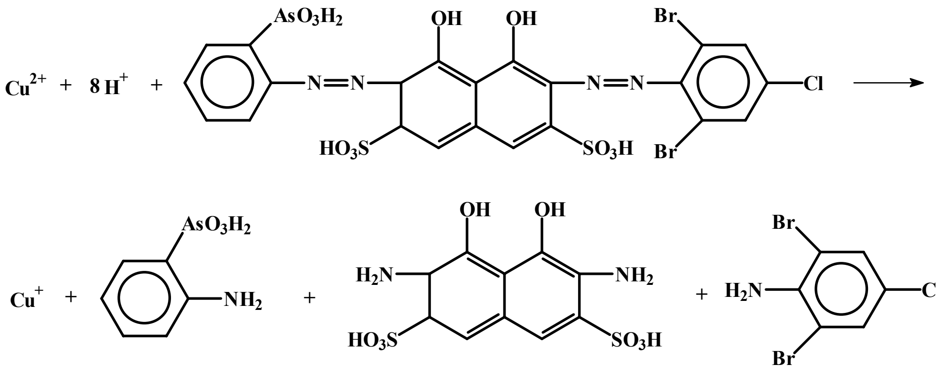
Stability of system: Under the optimum conditions the stability experiments of system were made. When the variation of ΔA was not more than ± 5 %, the system was considered to be stable. The experimental results showed that the stable time of the system was 7 h.

Calibration curve, precision and detection limit: A calibration curve for copper was constructed under the optimum conditions. A solution containing 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.2 µg of copper(II) was transferred into a series of 25 mL comparison tubes. Then, the operation was made according to the analytical procedure. A linear relationship between ΔA and final concentrations of copper(II) over the range of 0.1-1.2 µg/25 mL was found with an equation $\Delta A = 0.2032\ C$(C: µg/25 mL) - 0.0120 ($\gamma = 0.9940$), where C is the concentration of copper(II) in µg in a 25 mL of solution and γ is the correlation coefficient, respectively. The detection limit and quantitation limit of the copper determination were found to be 3.2 and 9.7 ng/mL, respectively, which was calculated by multiplying the standard deviation of eleven replicate measurements of absorbance for the reagent blank by three and dividing by the slope of the linear calibration curve. The relative standard deviation for eleven replicate determinations of 40 ng mL^{-1} of copper is 2.7 %. This indicates that the method has very good reproducibility. The precision of the method for real samples was checked by repetitive analyses (n = 11) of two samples.

Effect of coexisting ion: Under the optimum experimental conditions the effect of coexisting ions was also made. When 1.0 µg of copper(II) was determined in a 25 mL of solution and a relative error did not exceed ± 5 %, the allowable amounts of various coexisting ions (in mass multiple, m/m) were as follow: NH_4^+ (2000), SO_4^{2-} (1500), NO_3^- (1000), Cl^- (300), F^- (200), Mo^{6+} (150), Zn^{2+} (100), Ag^+, Mg^{2+}, Sr^{2+}, Cd^{2+} (50); Ca^{2+}, Mn^{2+} (20); Bi^{3+} (10), Br^- (2), Ni^{2+}, Pb^{2+}, Eu^{3+}, Ce^{4+}, Th^{4+}, Cr^{6+}, NO_2^- (1), Cr^{3+}, Y^{3+} (0.1); Co^{2+}, I^- (0.02); Fe^{3+} (0.01).

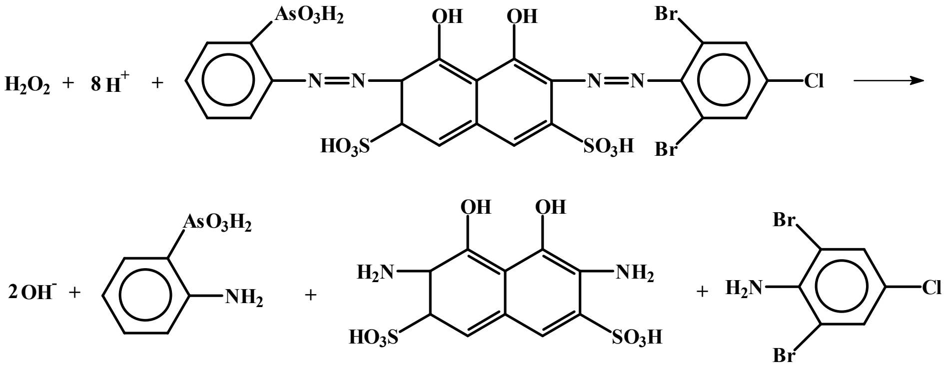
Mechanism of reaction: In this article, DBC-arsenazo was used as a chromogenic agent, H_2O_2 was an oxidant, Cu(II) was a catalyst. Based on the principle of catalytic reaction[11], the reaction mechanisms are proposed as follow:

Catalytic reaction progresses according to the following formula:



$$2Cu^+ + H_2O_2 \longrightarrow 2Cu^{2+} + 2OH^-$$

Non-catalytic reaction progresses according to the following formula:



Analysis of sample: The proposed method has already been successfully applied to the determination of copper in two water samples. The results showed (Table-1) that the results determined by the present procedure were in agreement with those by atomic absorption spectrometry. The relative standard deviation of 11 replicate determinations of copper in real samples with the proposed procedure was 3.6-4.8 %. The recovery of the method was between 99.8-100.5 %. The analytical results were quite satisfactory.

TABLE-1
ANALYTICAL RESULTS OF SAMPLES

Sample	Found (ng g^{-1})	Average (ng g^{-1})	RSD (%)	Added (μg/25 mL)	Recovery (μg/25 mL)	Recovery (%)	AAS method (ng g^{-1})
Tap water	24.1, 22.6, 25.1, 24.1, 23.1, 23.1, 25.6, 24.1, 23.6, 24.1, 24.6	24.1	4.8	0.400	0.402	100.5	24.0
Lake water	16.8, 17.0, 16.0, 16.5, 16.3, 17.2, 16.2, 16.0, 16.5, 16.5, 16.8	16.5	3.6	0.400	0.399	99.8	16.5

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