Catalytic Spectrophotometric Determination of Ultra Trace-level Copper(II) with Indigo Carmine

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In this paper, a novel kinetic spectrophotometric method for the determination of ultra trace Cu(II) was developed. This method was based on catalytic action of Cu(II) on the oxidation of indigo carmine by ammonium persulfate in $Na_2B_4O_7$-HCl buffer solution (pH = 9.09) and in presence of the surfactant-TritonX-100. Effects of some factors on the reaction speed were investigated in this study. It was observed that the concentration of Cu(II) was linearly correlating to ΔA in the range of 2.0×10^{-10}-1.6×10^{-9}g/mL for Cu(II) in this method. The detecting limit of the proposed method was 1.8×10^{-11}g/mL. This system was a first-order reaction for Cu(II). The apparent rate constant was 3.19×10^{-4} s^{-1} and the apparent activation energy was 112.5 kJ/mol in this system. Most of the foreign ions did not interfere with the determination and the interferences of Fe(III) and Al(III) could be masked by F$^-$. The proposed method was applied to the determination of ultra trace-level copper(II) in real samples with satisfactory results.

Key Words: Kinetic spectrophotometric method, Environmental analysis, Copper, Indigo carmine.

INTRODUCTION

There is a wide distribution of copper in nature. Copper is an indispensable microelement to human beings, animals and plants. It plays an important role in the metabolism. But excessing amount of copper can do harm to people᾽s health. The toxicity of copper relates to its form. Ionic copper is more toxic than complex copper. Therefore, the research of analytical method of copper is concerned by people all the time. There are some reports on the catalytic spectrophotometric methods for the determination of copper in recent years. The catalytic kinetic spectrofluorimetric method is an ideal method because of its high sensitivity, without using precious instruments and no toxic organic solution[1-11]. In this paper, a new catalytic spectrophotometric method was described for the determination of ultra trace amounts of Cu(II). This method was based on catalytic action Cu(II) on the oxidation of indigo carmine (IC) by ammonium persulfate in the $Na_2B_4O_7$-HCl buffer solution (pH = 9.09) and in the presence of surfactant-TritonX-100. This method was very rapid, simple, inexpensive, selective and high sensitive. The copper detecting limit of this method was 1.8×10^{-11}g/mL. The sensitivity of this proposed method was better than that of other catalytic spectrophotometric methods[5,6] and was also much better than that of other classical catalytic spectrophotometric methods.

EXPERIMENTAL

The Cu(II) standard solution (1.000 g/L) was prepared by dissolving 0.9824 g $CuSO_4 \cdot 5H_2O$ (spectrographically pure) in 250 mL water and it was diluted to appropriate concentration when needed. Tween-20 solution was purchased from Shanghai Chemicals. 1.00×10^{-3} mol/L indigo carmine (IC) solution; $Na_2B_4O_7$-HCl buffer solution whose pH value is 9.09; 0.020 mol/L $(NH_4)_2S_2O_8$ solution; 10 % Tween-20 solution. Secondly distilled water and analytical reagent grade chemicals were used throughout.

The absorption spectra were recorded on a Shimadzu model UV2100 UV-VIS recording spectrophotometer, Japan. The absorbance measurements were made by a 722-type spectrophotometer (Sichuan No. 9 instruments, China). pH value was measured on a PHS-3C pH meter (Shanghai Analytical Instruments, China).Temperature was controlled by a CS502-1 thermostat (Chongqing Experimental Instruments, China).

Recommended procedure: The reactors are two comparison tubes with lids. 1 mL $Na_2B_4O_7$-HCl buffer solution (pH = 9.09), 4 mL 0.020 mol/L $(NH_4)_2S_2O_8$ solution, 4 mL Tween-20 solution and 1.5 mL indigo carmine were put into the two tubes, respectively. Then a certain dosage of Cu(II) solution was put into one of them and a mark was made on this tube. The solutions in both tubes were diluted with water to 25.00

mL and were left in (35 ± 0.5) ºC thermostat for 10 min. Then a portion of the solutions was transferred into a 1 cm glass cell and was measured the absorbance of both reaction mixtures at 608 nm. A_0 is absorbance of solution without copper; A is absorbance of the solution with copper. Then the value of ΔA was calculated as following: $\Delta A = (A_0-A)$.

RESULTS AND DISCUSSION

Absorption spectra: A series of solutions were prepared. The absorption spectra of these solutions were measured in the wavelength range of 400-700 nm. The absorption spectra were given in Figs. 1 and 2, from which it can be seen that these absorption spectra reach their maximum at 608 nm both catalyzed and uncatalytic reaction systems and their difference also reaches its maximum at 608 nm. As a result, 608 nm was selected as the measuring wavelength. As shown in Figs. 1 and 2, by adding Tween-20, the ΔA of the reaction system can be promoted obviously at 608 nm.
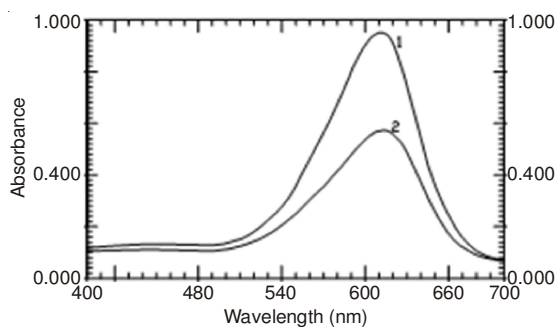

Fig. 1. Absorption spectra (without surfactant). (1) buffer solution + $(NH_4)_2S_2O_8$ + indigo caramine. (2) buffer solution + $(NH_4)_2S_2O_8$ + IC + 5.0 ng Cu(II)
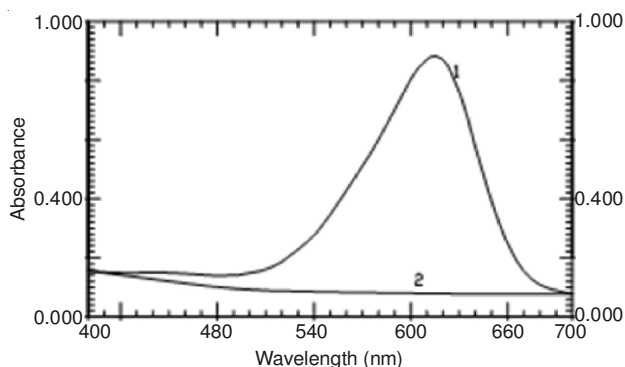

Fig. 2. Absorption spectra (with surfactant). (1): buffer solution + $(NH_4)_2S_2O_8$ + indigo caramine + Tween-20. (2) buffer solution + $(NH_4)_2S_2O_8$ + IC + Tween-20 + 5.0 ng Cu(II)

Effect of buffer solutions: The effects of 9 kinds of buffer solutions on ΔA were studied. 9 kinds of buffer solutions were as follows: CH_3COOH-CH_3COONa, H_3PO_4, NH_4Cl-NH_3, hexamethylene tetramine-hydrochloric acid, HCl, potassium acid phthalate, HAc-NH_4Ac, H_2SO_4, $Na_2B_4O_7$-HCl and ($Na_2B_4O_7$-NaOH). Then the results of research indicated that when $Na_2B_4O_7$-HCl and ($Na_2B_4O_7$-NaOH) was used as buffer solution, ΔA reached its maximum. A series of $Na_2B_4O_7$-HCl buffer solutions were prepared when their pH value of buffer solution is in the range of 7.62-9.51.

The effect of pH value of buffer solution (7.62-9.51) on ΔA was studied. The results were given in Fig. 3, which shows that ΔA reaches its maximum when the pH is between 8.91 and 9.24 and ΔA has a perfect stability. So $Na_2B_4O_7$-HCl (pH = 9.09) buffer solution was selected as the optimum experimental condition.
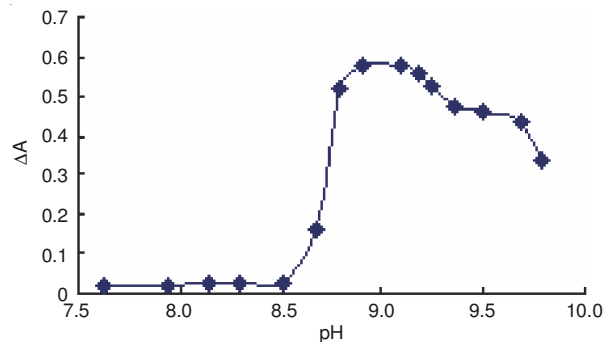

Fig. 3. Curve of acidity

Under the experimental conditions, the effect of the dosage of buffer solution on ΔA was studied. The results of research were given in Fig. 4. It was observed from Fig. 4 that ΔA reaches its maximum when the dosage of $Na_2B_4O_7$-HCl is between 0.75 and 1.25 mL and has a preferable stability. So the 1.0 mL dosage of $Na_2B_4O_7$-HCl buffer solution was selected as the optimum experimental condition.
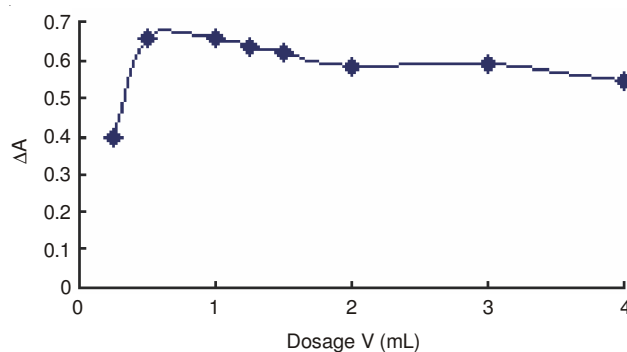

Fig. 4. Effect of buffer solution

Effect of oxidants: The effects of 4 kinds of oxidants on ΔA were studied. 4 kinds of oxidants were as follows: hydrogen peroxide, ammonium persulphate, potassium periodate and potassium bromate. It was found that ΔA reached its maximum when ammonium persulfate was selected as the oxidant.

The optimum dosage of oxidant was chosen through experiments. The results of research were given in Fig. 5. As shown in Fig. 5, when the dosage of oxidant is between 2 and 6 mL, ΔA is very stable and has a quite large value. Therefore, the dosage 4.0 mL of ammonium persulfate was selected as the optimum experimental condition.

Effect of indicators: When the other reaction conditions were fixed, the effect of indicators on ΔA was studied. The results of research were given in Fig. 6. It was observed from Fig. 6 that when the dosage of IC is between 1.50 and 2.25 mL, ΔA has a preferable value. So the dosage of 1.5 mL of IC was selected as the optimum experimental condition.
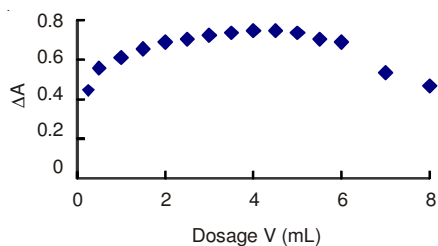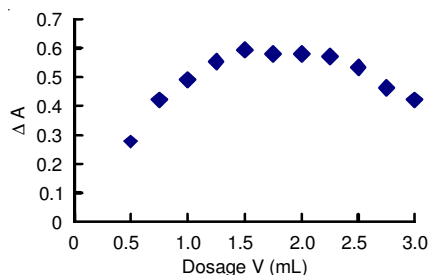
Fig. 5. Effect of oxidation

Fig. 6. Effect of indicator

Fig. 8. Effect of temperature

Fig. 9. Effect of time

Effect of surfactants: When the other reaction conditions were fixed, the effect of 5 kinds of surfactants indicators on ΔA was studied. 5 kinds of surfactants indicators as follows: TritonX-100, CTMAB, 2,2'-dipyridine, OP, Tween-20. When CTMAB was added, the solution became cloudy, so CTMAB could not be used. When Tween-20 was used as the surfactant, ΔA had its biggest value. So Tween-20 was selected as the optimum experimental condition.

The effects of the dosage (1-10 mL) of Tween-20 on ΔA were given in Fig. 7, which shows that when the dosage of Tween-20 is between 4 and 6 mL, ΔA reaches its maximum and has a preferable stability. So the 4 mL dosage of Tween-20 was selected as the optimum experimental condition.
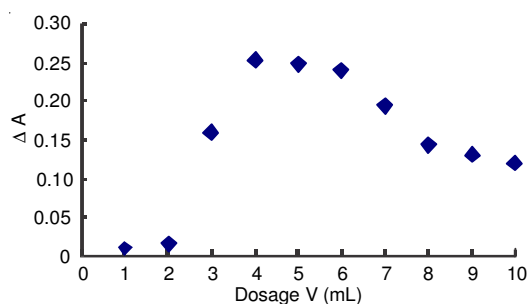

Fig. 7. Effect of surfactant

Effect of temperature and reaction time: When the other reaction variables were fixed, the effect of temperature on ΔA was studied. The results were given in Fig. 8. Experimental results show that when the temperature is ranging from 21 to 35 ℃, ΔA is linear with the temperature. When the temperature is higher than 35 ℃, ΔA begins to decrease. So 35 ℃ was selected as the optimum reaction temperature.

When the other reaction variables were fixed, the effect of reaction time on ΔA was studied. The results were given in Fig. 9. It can be seen from Fig. 9 that ΔA is linear with the time when the reaction time is from 3-9 min, However, when reaction time is longer than 9 min, ΔA begins to decrease. So the 8 min was selected as the optimum reaction time.
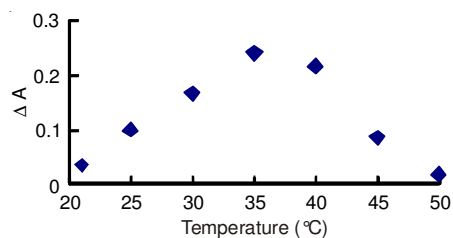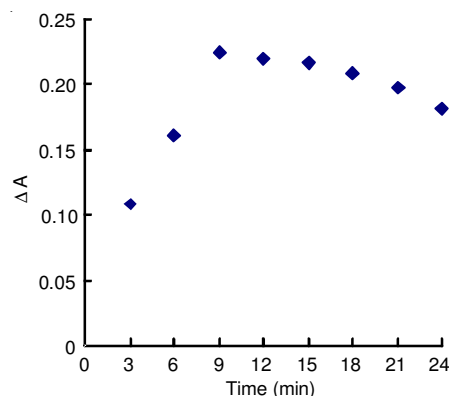
Calibration: Under the optimum conditions mentioned above, the concentration of Cu(II) was linearly correlating to ΔA in the range of 5 ng/25 mL-40 ng/25 mL for Cu(II). The regression equation was: $\Delta A = 0.01325 C_{Cu^{2+}}$ (ng/25 mL) 0.1033. The correlation coefficient of the regression equation was equal to 0.9998. The detection limit of the method was calculated by 3s/b method. The detection limit of Cu(II) was 1.8×10^{-11} g/mL.

Selectivity: When the dosage of Cu(II) was 0.0050 μg/ 25 mL and the error was controlled between -5 and + 5 %, more than 20 substances (cations or anions) were studied for possible interference substances in the determination. The possible interference substances and their permitted amounts as follows: K^+, Na^+, NH_4^+, Cl^- (10.0 mg/25 mL); SO_4^{2-}, NO_3^- (5.0 mg/25 mL); Ac^- (2 mg/25 mL); CO_3^{2-} (1.0 mg/25 mL); Br^-, Ca(II), Ba(II) (0.80 mg/25 mL); W(VI), Si(VI) (0.50 mg/ 25 mL); NO_2^-, I^-, Mo(VI) (0.20 mg/25 mL), As(VI) (0.10 mg/ 25 mL); Pb^{2+} (0.060 mg/25 mL); F^-, Ag^+, Hg(II) (0.050 mg/25 mL); $C_2O_4^{2-}$, Cr(VI) (0.020 mg/25 mL) Zn(II), PO_4^{3-} (0.010 mg/25 mL); Mg(II), Mn(II), Cd(II) (0.0020 mg/25 mL); Fe(III) (0.0010 mg/25 mL, 0.025 mg/25 mL*); Al(III) (0.00050 mg/ 25 mL, 0.0050 mg/25mL*). (* indicates the permitting concentration in the presence of 50 μg/25mL F^-).

Applied for real samples: The present procedure was applied to the determination of copper in tap water, underground sewage, water in JiaLing River, flocculant CPF110, flocculant CPF130, milk powder and apple.

Tap water, water in JiaLing river and underground sewage were filtered first and their pH values were controlled in the range of 5-6. A certain amount of flocculant CPF110 and flocculant CPF130 were heated in electric heater first. And when there were no evolution of white fume any more, the samples of mixtures were moved into muffle furnace and the temperature was adjusted in the range of 600-700 ℃. After ashing for 6 h, the samples of mixtures were moved out of

TABLE-1
DETERMINATION OF SAMPLES

Sample	Proposed method					AAS
	Found	RSD (%) (n = 6)	Added	Found	Recovery (%)	
CPF110	5.44	1.69	5.00	5.11	102	5.4[a]
CPF130	5.22	1.21	5.00	5.05	101	5.2[a]
Milk powder	0.0301	1.35	5.00	5.05	101	0.03[a]
Underground sewage	0.669	0.87	5.00	5.01	100	0.67[b]
Water in JiaLingJiang river	0.587	2.15	5.00	4.86	97.2	0.59[b]
Tap water	0.524	2.04	5.00	4.93	98.6	0.52[b]
Apple	0.0401	1.33	5.00	5.09	101	0.04[1]

[a]Unit: µg/g, [b]Unit: µg/mL.

muffle furnace and cooled down. Then another 10 mL 1:1 HCl was added into the solution and the mixtures were poured into a beaker. The samples were gently heated to boiling. And when the reaction processed completely and the overabundance HCl was removed. After cooling down and filtering samples, the filtrates were transferred into 50 mL volumetric flask. About the procedure for the pretreatment of milk powder and apple, please refer to Reference[12]. Before the determination of the listed samples, F^- was needed to add in as a masking reagent.

The proposed method and AAS method were applied to the determination of copper(II) in these solutions, respectively. The results were listed in Table-1.

Probe into the reaction mechanism: The catalytic process of Cu(II) on the oxidation of indigo carmine (IC) by ammonium persulfate in $Na_2B_4O_7$-HCl buffer solution (pH = 9.09) and in the presence of surfactant-TritonX-100 could be indicated as follows:
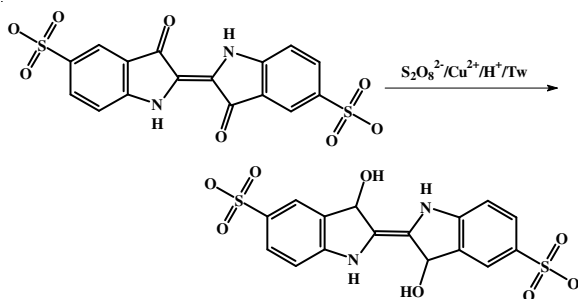
Kinetic equation of this reaction is:

$$-\frac{dC_{IC}}{dt} = kC_{S_2O_8^{2-}} C_{H^+} C_{Tween} C_{Cu^{2+}}^{\alpha} C_{IC} \quad (1)$$

Because the concentration of $(NH_4)_2S_2O_8$, Tween-20, indigo caramine were over dosed; in addition, concentration of H^+ was unchanged in the buffer solution; their concentration could be considered to be stable and regarded as constants. So the reaction eqn. 1 could be simplified as:

$$-\frac{dC_{IC}}{dt} = kC_{Cu^{2+}}^{\alpha} \quad (2)$$

The only parameter to be determined is the value of α in this reaction equal (2).

The ΔA-t curves for different Cu(II) concentration was drawn in the activated system (Fig. 10). Then the slope m was calculated. The slope of the regression curve α was gained by the regression of $-\log m$ to $-\log Cu^{2+}$. By calculating, α was equal to 1. So the catalytic reaction for Cu(II) was a first order reaction.

ΔA was linearly correlating to reaction time t when the reaction time was between 3 and 9 min. This linear part of the curve was dealt with by the least square method. Then the regression equation to the activated system was gained. The regression equation was: ΔA = 0.01916t + 0.04969. The correlation coefficient of the regression equation was equal to 0.998. The apparent rate constant of this catalytic reaction could be calculated with 3.19×10^{-4} s^{-1}.

ΔA was linearly correlating to T when the reaction temperature was between 21 and 35 ºC. The regression equation of -ln ΔA to 1/T was gained in the temperature range mentioned above to the activated system. The regression equation of -ln ΔA to 1/T was -ln ΔA = 13.5289 × 103/T + 42.7733. The correlation coefficient of the regression equation r was equal to 1.0105. The apparent activation energy E_a of this reaction could be calculated according to Arrhenius formula. The apparent activation energy E_a was equal to 112.5 KJ mol^{-1}.

Conclusion

The proposed kinetic-catalytic photometric method was simple, rapid, inexpensive, sensitive and selective for the determination of copper. The determination limit of Cu(II) was 1.8×10^{-11} g/mL.

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