Investigation of properties of copper, ferrous complexes with 1-(5-bromo-2-pyridylazo)-2-naphthol-6-sulphonic acid and application of substitution reaction in metallic complex to selective determination of trace amounts of metal

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Abstract

The report was the first to establish the new method for the selective determination of trace amounts of metal using the substitution reaction in metallic complex. The reactions between copper(II) and 1-(5-bromo-2-pyridylazo)-2-naphthol-6-sulphonic acid (BPANS) and between ferrous(II) and BPANS at pH 3.5 were studied. In absence of any masking reagent, the recommended method was selective in the determination of trace amounts of copper with Fe–BPANS complex as chromogenic reagent because copper(II) can substitute Fe from Fe–BPANS complex to form Cu–BPANS complex. The ordinary spectrophotometric method was unsuitable to the substitution reaction because the excess of Fe–BPANS complex had the high absorption and affected seriously the absorption of Cu–BPTANS complex. The spectral correction principle may eliminate the above influence to give the simple determination of the composition ratio, stepwise absorptivity (ε) and stability constant (K) of metal complex. For analysis of samples, the recovery of copper was between 96.5 and 106% with R.S.D. less than 5%. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Spectral correction principle; Substitution reaction in metallic complex; Determination of copper; 1-(5-Bromo-2-pyridylazo)-2-naphthol-6-sulphonic acid (BPANS)

1. Introduction

Copper often exists in wastewater, ore, metal material and so on. The chromogenic reagents, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [1], dithizone, di-2-pyridyl-methanone-2-(5-nitropyridyl) hydrazone [2] and others were ever applied to the determination of copper by spectrophotometry. The synthesis of the ligand, 1-(5-bromo-2-pyridylazo)-2-naphthol-6-sulphonic acid (BPANS) was ever reported [3] with the following structure.
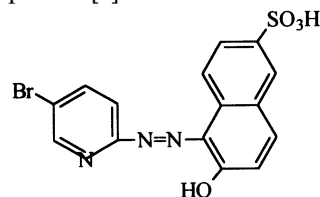
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It was ever applied to the titrimetric determination of ferrous and zinc [4,5]. In this work, the substitution reaction between copper and Fe–BPANS complex at pH 3.5 was found and applied to the determination of trace amounts of copper. The reaction was highly selective because of the presence of plenty of ferrous in solution. None of the other metallic ions formed complex except for Cu(II) even if in the masking reagent was absented. The new principle, spectral correction theory [6] was ever applied to the analysis of many metal complexes solution [7–9]. It was used instead of the ordinary spectrophotometry because of the high absorption of the excess of Fe–BPANS complex. It was able to eliminate the absorption interference of free ligand or reactant and give out the real absorbance of the complex. By means of this method, the determination of properties of Fe–BPANS and Cu–BPANS complexes was made such as complex ratio, stepwise absorptivity and stability constant. The recommended method was more acceptable in principle and simpler in operation than the classical method for example the molar ratio [10], the continuous variation [11] the equilibrium movement [12], etc. Results showed that complexes Fe(BPANS)$_3$ and Cu(BPANS)$_2$ were formed in this study, their cumulative stability constants being 3.46×10^{15} and 2.10×10^{11}, their real (not apparent) absorptivities being 1.87×10^4 at 550 nm and 1.94×10^4 at 565 nm, respectively. For the analysis of samples, the recovery of copper was between 96.5 and 106% with R.S.D. less than 5%. The detection limit of copper was equal to 0.02 mg l^{-1}.

2. Principle

From the following expression is developed for the determination of the real absorbance (A_c) of metal (M) complex (ML$_\gamma$) produced with a ligand (L).

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha\beta}$$

The terms, ΔA and $\Delta A'$ are the absorbances of the reacted solution between M and L at wavelengths λ_2 and λ_1 against the reagent blank, respectively. The coefficients, α and β are named correction factors and they are able to be measured from only ML$_\gamma$ solution and L solution then computed as follows.

$$\alpha = \frac{\varepsilon_{ML_\gamma}^{\lambda_1}}{\varepsilon_{ML_\gamma}^{\lambda_2}} \text{ and } \beta = \frac{\varepsilon_{L_\gamma}^{\lambda_1}}{\varepsilon_{L_\gamma}^{\lambda_2}}$$

The terms $\varepsilon_{ML_\gamma}^{\lambda_1}$, $\varepsilon_{ML_\gamma}^{\lambda_2}$, $\varepsilon_{L_\gamma}^{\lambda_1}$ and $\varepsilon_{L_\gamma}^{\lambda_2}$ are the molar absorptivities of ML$_\gamma$ and L at wavelengths λ_1 and λ_2, respectively.

The amount ratio (γ') of L to complex M in their reaction may be expressed as follows:

$$\gamma' = \eta \frac{C_L}{C_M} \text{ where } \eta = \frac{\alpha\Delta A - \Delta A'}{(1 - \alpha\beta)A_0'}$$

The term η indicates the reacted percentage of L and δ the cell thickness (cm). The factors, C_M and C_L are the concentrations (mol l^{-1}) of M and L in the beginning. A_0' is the absorbance of the blank reagent measured at wavelength λ_1. If γ' reaches maximum and remains constant, it was thought that $\gamma = \gamma'$ where γ is a natural number and it is named the stoichiometric ratio of the complex produced. In addition, the following expression was established for the stepwise stability constant (K_n) of complex ML$_\gamma$ from the reaction: ML$_{n-1}$ + L → ML$_n$. For this purpose, such a M–L solution must be prepared to form the complex ratio γ' between $n-1$ and n and studied successively.

From each K_n the cumulative constant (K) of complex ML$_\gamma$ is able to calculated from the following

$$K_n = \frac{\gamma' + 1 - n}{(n - \gamma')(C_L - \gamma'C_M)}$$

expression: $K = K_1 \times K_2 \times \ldots \times K_n \ldots \times K_\gamma$. In addition, from such an M–L reaction the stepwise absorptivity (real $\varepsilon_{ML_n}^{\lambda_2}$ not apparent $\varepsilon_a^{\lambda_2}$, $n = 1, 2, \ldots, \gamma$) of complex ML$_\gamma$ may be expressed as follows:

$$\varepsilon_{\mathrm{ML}_n}^{\lambda_2} = \frac{A_c}{\delta CM(\gamma' + 1 - n)} - \frac{n - \gamma'}{\gamma' + 1 - n} \varepsilon_{\mathrm{ML}_{n-1}}^{\lambda_2}$$

where all terms have the same meanings as the above. In fact, the beta-correction method was one of the dual-wavelength spectrophotometric method but it was different from the others [13–15] in principle and in operation.

3. Experimental

3.1. Apparatus and reagents

Absorption spectra were recorded with an UV–VIS 265 spectrophotometer (Shimadzu, Japan) in 10-mm glass cells.

Standard Fe(II) and Cu(II) solutions, 1000 mg 1^{-1} were both prepared with 1.000 g of their high-purity metal by dissolving with hydrochloric acid or nitric acid and diluted to 1000 ml.

Standard Fe(II) and Cu(II) work solutions, both 10.0 mg 1^{-1} must be prepared daily.

BPANS ligand solution, 1.00 mmol 1^{-1} BPANS was prepared by dissolving 0.2040 g of 1-(5-bromo-2-pyridylazo)-2-naphthol-6-sulphonic

acid (BPANS, Shanghai Changke Reagents) in 100 ml of acetone (A. R., Shanghai Chemical) then diluting to 500 ml with non-ionic water. It should be stored in a dark bottle and at less than 5°C.

Fe–BPANS chromogenic reagent solution was prepared by mixing 100 ml of 5% ammonium ferrous sulfate (A. R., Beijing Chemical) with 100 ml of 0.204% BPANS acetone solution and adding 10 ml of pH 3.5 buffer solution then diluting to 500 ml with non-ionic water. The final solution should contain 1.00 mmol 1^{-1} Fe(BPANS) complex because Fe(II) concentration was much more than BPANS where the free BPANS concentration approached to zero. This solution was used to react copper (II) so as to carry out the selective determination of trace amounts of copper.

The buffer solution, pH 3.5 was prepared with potassium acid phthalate (A. R., Shanghai Chemical) for adjusting the pH of the reaction solution.

3.2. Recommended procedures

A known volume of a sample solution containing less than 40.0 μg of Cu(II) was taken in a 25-ml volumetric flask. Added 2.5 ml of pH 3.5 buffer solution and 1.5 ml of Fe–BPANS solution. Diluted to volume and mixed well. Kept in 40°C water bath for over 10 min then cooled. Measured absorbances at 475 and 565 nm against a reagent blank (no containing copper), respectively.

4. Results and discussion

4.1. Absorption spectra

Fig. 1 showed the absorption spectra of BPANS, Fe–BPANS, Cu–BPANS and Cu–Fe–BPANS solutions at pH 3.5. From curves 2 and 3, the maximal absorption of Fe–BPANS complex were at 500 nm and that of Cu–BPANS complex at 565 nm. However, the wavelengths should be
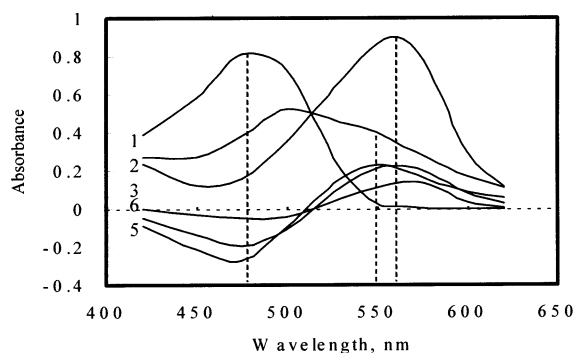

Fig. 1. Absorption spectra of BPANS, Fe–BPANS and Cu–BPANS complex solutions at pH 3.5: 1, 1.50 μmol BPANS; 2, only Fe–BPANS complex solution; 3, only Cu–BPANS complex solution; 4, Fe (20 μg)–BPANS reaction solution; 5, Cu (20 μg)–BPANS reaction solution; and 6, Cu (20 μg)–(Fe–BPANS) substitution solution. 1–3 against water and 4–6 against reagent blank.
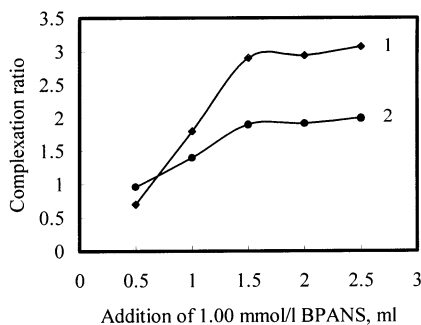
Fig. 2. Effect of the addition of BPANS solution on γ': 1, Fe (20 μg)–BPANS solution; and 2, Cu (20 μg)–BPANS solution.

selected such that the difference in absorbances approached to maximum: 475 and 550 nm in Fe–BPANS complex solution from curve 4 and 475 and 565 nm in Cu–BPANS complex solution from curve 5. Therefore, the three wavelengths, 475, 550 and 565 nm were used in the determination of the properties of two complex solutions. By comparing the peak wavelength of curve 4 with that of curve 5, it was indubitable that the ordinary spectrophotometric method was limited due to the wavelengths difference only 15 nm. From curve 6, the valley absorption wavelength 475 nm and the peak absorption wavelength 565 nm should be selected as the work wavelengths in the reaction of copper (II) to substitute Fe(II) from Fe–BPANS complex and in the determination of trace amounts of copper (II). The coefficients, β and α was calculated as follows: $\beta^{L}_{550/475} = 0.033$, $\beta^{L}_{565/475} = 0.011$ from curve 1, $\alpha^{FeL}_{475/550} = 0.960$, $\alpha^{FeL}_{475/565} = 0.762$ from curve 2 (use in the determination of trace amounts of copper) and $\alpha^{CuL}_{475/565} = 0.182$ from curve 3. The following expressions were established: $A_c = 1.03(\Delta A - 0.033\Delta A')$ at 550 nm for Fe–BPANS reaction and $A_c \approx \Delta A - 0.011\Delta A'$ at 565 nm for Cu–BPANS reaction. The two expressions were used in the determination of properties of Fe and Cu complexes with BPANS. The following expression was used in the selective determination of trace amounts of copper: $A_c = 1.16(\Delta A - 0.762\Delta A')$ at 565 nm using Cu–(Fe–BPANS) substitution reaction.

4.2. Effect of pH

By varying pH of solution, the effect on absorption of the complex solutions indicated that the absorption of Cu–BPANS complex solution remained almost constant between pH 3.5 and 10.5. However, the absorption of Fe–BPANS complex solution decreased rapidly at pH over 8.5. The further experiments still found that other metallic ions formed the similar complex and interfered the absorption of Cu–BPANS complex if pH of solution was more than 5, for example nickel(II), cobalt(II), zinc(II), cadmium(II) and so on. Therefore, the buffer pH 3.5 was selected in this work.

4.3. Determination of properties of two complexes

By varying the addition of 1.00 mmol 1^{-1} BPANS, the effect indicated that it was difficult for the complex ratio of Fe or Cu to BPANS to be calculated accurately with the molar ratio method by the reason of unclearness of the inflexion point. The peak absorption and valley absorption of Fe–BPANS and Cu–BPANS solutions approached to maximum when the addition of 1.00 mmol 1^{-1} BPANS was over 1.5 ml. The term, γ' of each solution was calculated from equation described in principle and its was shown in Fig. 2. From curve 1, γ' remained the maximum 3 in Fe–BPANS reaction when the addition of 1.00 mmol 1^{-1} BPANS was over 1.5 ml. Therefore, the complex Fe(BPANS)$_3$ was formed. With the same analysis, from curve 2, Cu(BPANS)$_2$ was formed, too.

The following solutions were prepared for the determination of stepwise absorptivity and stability constant of Fe–BPANS and Cu–BPANS complexes: 20.0 μg Fe(II) with 0.40, 0.80, 1.20 μmol BPANS and 20.0 μg Cu(II) with 0.30, 1.00 μmol BPANS. Three replicated determinations of each solution were carried out. The mean stepwise absorptivity (ε) and mean stability constant (K_i) of Fe–BPANS and Cu–BPANS complexes were calculated according to the equations described in principle and the results were listed in Table 1. Their R.S.D. were all less than 10%. The cumulative stability constant of Fe(BPANS)$_3$ and Cu(B-

PANS)$_2$ was equal to 3.46×10^{15} and 2.10×10^{11}, respectively in ionic strength 0.025 and at room temperature 10°C. From Table 1, the 1st-step stability constant of Fe(BPANS)$_3$ was much less than that of Cu(BPANS)$_2$. Therefore, trace amounts of Cu(II) substituted Fe from Fe(B-

Table 1
Determination of stepwise stability constant and absorptivity ($l \ mol^{-1} \ cm^{-1}$) of complex Fe(BPANS)$_3$ and Cu(BPANS)$_2$ at pH 3.5, in ionic strength 0.025 and at room temperature 10°C

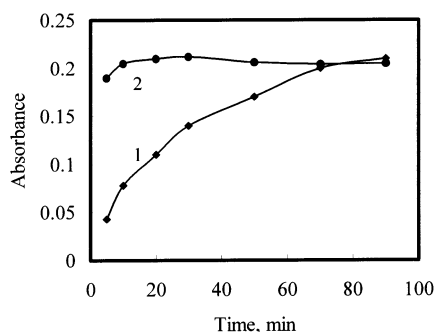| nth	Fe(BPANS)$_3$		Cu(BPANS)$_2$	
	K_n	ε_r at 550 nm	K_n	ε_r at 565 nm
1st	5.77×10^5	5.93×10^3	1.11×10^7	1.64×10^4
2nd	1.58×10^5	1.24×10^4	1.89×10^4	1.94×10^4
3rd	3.80×10^4	1.87×10^4		

Fig. 3. Effect of the reaction time on real absorbance (A_c) of Cu–BPANS complex in Cu(20 μg)–(Fe–BPANS) solution at 565 nm: 1, at room temperature; and 2, in 40°C water bath.
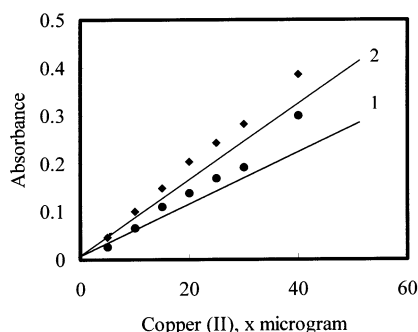

Fig. 4. Standard curves for the determination of Cu(II) using the substitution reaction between Cu(II) and Fe(BPANS) complex at pH 3.5: 1, ΔA; 2, A_c, both at 565 nm.

PANS)$_3$ complex to form the new complex Cu(B-PANS)$_2$. Therefore, the above substitution reaction was applied to the determination of trace amounts of copper so as to improve greatly the selectivity. The chromogenic reagent, Fe(BPANS) complex solution, 1.00 mmol l^{-1} was prepared by adding plenty of Fe(II) in 1.00 mmol l^{-1} BPANS.

4.4. Effect of addition of Fe–BPANS reagent

The effect of the addition of Fe–BPANS solution on the absorbance of Cu(II) complex solution indicated that the peak and valley absorption of the reaction solution remained maximum when the addition of 1.00 mmol l^{-1} Fe(BPANS) solution was over 1.0 ml. Therefore, 1.5 ml of the chromogenic reagent solution was used in the determination of trace amounts of copper. The effective percentage of Fe(BPANS) was only 20% in the selected addition, 1.5 ml of Fe(BPANS) solution. Therefore, 80% chromogenic reagent was excess and free in solution. Therefore, it was indubitable for such more excess of Fe(BPANS) to affect the absorption of Cu–BPANS complex. The ordinary spectrophotometry gave the unacceptable error in the determination of trace amounts of copper.

4.5. Effect of time

Fig. 3 showed that the effect of the reaction time on absorption of Cu–(Fe–BPANS) reaction solution at room temperature (10°C) and in warm water. It took over 1 h to complete this reaction at room temperature but only 10 min if placed in 40°C warm water bath.

4.6. Calibration graph

A series of standard Cu (0–40.0 μg per 25 ml) solutions were prepared and the absorbance of each was measured at 475 and 565 nm. The real absorbance at 565 nm, A_c was computed and its curve was shown in Fig. 4. All points around curve 2 were more linear than these around curve 1. Also, the slope of curve 2 was more than that of curve 1. Therefore, the beta-correction method gave the better precision and higher sensitivity

Table 2
Determination of trace amounts of copper in practical samples by the substitution reaction between copper and Fe–BPANS complex at pH 3.5

Sample	Added	Found	Recovery (%)
Wastewater (mg l^{-1})	0	0.108	
		0.100	
		0.115	
		0.112	
		0.104	
		0.104	
		Average 0.107 (0.114^a)	
	0.200	0.317	105
		0.300	96.5
		0.319	106
Ore (mg g^{-1})	0	18.2	
		18.8	
		17.5	
		Average 18.2 (16.9^a)	
	20.0	37.6	97.0
		38.1	99.5
		39.3	105

^{a} Average of two determinations by AAS.

than the ordinary spectrophotometry. The following equation was expressed: $A_c = 0.0096X$, which was used in the determination of trace amounts of copper.

4.7. Precision and detection limit

Ten replicate determinations of both standard solutions containing 5.00 and 20.0 μg Cu(II) were carried out. The R.S.D. were 2.4 and 1.2%, respectively. However, the R.S.D. were both over 8% from the ordinary spectrophotometry.

The formula, $L_{min} = kS_b/S$ was used to calculate the detection limit of copper (where k was often selected as 3, the sensitivity factor, S was equal to the slope of the above standard curve 2 and S_b indicated the S.D. of the replicated measurements of twenty reagent blanks). The result gave out the detection limit only 0.5 μg Cu(II) in 25 ml of solution (being 0.02 mg l^{-1}).

4.8. Effect of foreign ions

Because of the use of Fe(BPANS) complex as chromogenic reagent and the presence of a great deal of free Fe(II), the absence of masking reagent was recommended and none of the following ions affected the direct determination of 10 μg of Cu(II) ($< 10\%$ error): 10 mg of Cl$^-$, SO$_4^{2-}$, SO$_3^{2-}$, S$_2$O$_3^{2-}$, NO$_3^-$, NH$_4^+$, K(I), Na(I), Be(II), Ti(I), Ca(II), Mg(II); 1 mg of Al(III), Fe(III), Fe(II), Sn(II), Pb(II), V(V), Mo(VI), Cr(III), Cd(II), Mn(II), Ag(II) and 100 μg of Co(II), Ni(II), Hg(II).

4.9. Sample analyzed

As a test of the method, copper was determined in ore and wastewater. The results were listed in Table 2. By comparing the average with that by AAS, the recommended method was suitable to direct determination of trace amounts of copper in wastewater, ore and other samples. The recovery of standard copper (II) added in practical samples was between 96.5 and 106%. Therefore, copper was recovered completely. The RSD of six determinations of copper in wastewater was equal to 5%, which was less than the critical precision, 10%.

Acknowledgements

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