Asian Journal of Chemistry Vol. 10, No. 1 (1998), 23–2

Further Analysis of Copper Chelate Solution with Murexide

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The chelated reaction of copper(II) with murexide at pH 12 is further studied for analysis of characteristic factors of the chelate formed. Besides, the determination of trace amounts of copper in metal material and waste water is made in this part using β-correction principle. For this updated theory, to completely eliminate the effect of excess ligand in its Cu(II) chelated solution, the sensitivity, accuracy and precision are all improved for micro determination, but also it brings out the satisfactory result for analysis of the chelate characteristic factors including complexation ratio and practical molar absorptivity using spectrophotometric method. The results show that the chelate formed is expressed by Cu $(\text{murexide})_2$ and Beer's law obeyed over the concentration range 0–4.00 mg/L copper with the detection limit of copper 0.05 mg/L. The recovery is between 97.4 and 104% with the relative standard deviation less than 4.4%.

INTRODUCTION

Copper (Cu) often exists in metal materials and in some waste waters polluted by, *e.g.*, the metallurgical, electroplating and other industries. In the present spectrophotometric methods, trace copper has ever been determined with ligands including porphyrin[1], triphenylmethane[2], hydrazone[3], azo compounds[4], etc. The ligand, murexide, is sensitive and is used for the determination of calcium by EDTA titration.[5] It is not posible for the ordinary spectrophotometry to be used for the determination of trace amounts of copper because of the serious interference of excess murexide. In fact, the reaction of Cu with murexide is sensitive for the colour change and selective in the presence of F^- and citrate. The updated method named β-correction principle was established in 1994[6] and later it was applied widely for determination of trace amounts of metal ions.[7–12] It can eliminate completely the effect of excess of ligand from its metal chelated solution to obtain the real absorbance of the chelate.

In present work, we analyse Cu(II) chelate solution accompanying the determination of trace Cu(II). The sensitivity, precision and accuracy are much better than those obtained by the single wavelength method. Besides, the complexation ratio of Cu(II) to murexide is caculated to be 1 : 2, which is simpler in operation and more accurate in data than that obtained by the molar ratio method.[13]

Consider the following reaction example of ligand (R) with metal (Me) for illustrating the β-correction principle.

$$aR + bMe \rightarrow bMeR_\gamma + cR \qquad (1)$$

where a and b are the initial concentrations of ligand (R) and metal (Me), respectively, c is the concentration of excess R in the complexing solution, γ is t

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he complexation ratio of R to Me. At wavelength λ_2 the real absorbance (Ac) of chelate MeR_γ is expressed by the following equation:

$$Ac = (\Delta A - \beta\Delta A')/(1 - \alpha\beta) \qquad (2)$$

where ΔA and $\Delta A'$ are absorbances of the above solution at λ_2 and λ_1 against reagent blank, respectively. Both α and β are constants named correction coefficients. From Ac value the effective percentage for complexation (η%) of R and the complexation ratio (γ) of R to Me can also be calculated by the following expressions:

$$\eta = (Ac - \Delta A)/(A'_0 \cdot \beta) \times 100\% \qquad (3)$$

$$\gamma = 0.01 M_1 \eta\, V_0/M_2 \qquad (4)$$

where A'_0 is the absorbance of the reagent blank at λ_1, determined against water reference, M_1 is the molarity of R solution in mmol/L and M_2 is molar amount of Me in µmol at the beginning and V_0 is the addition of R solution in mL.

EXPERIMENTAL

Visible spectra were recorded with a Model 7230 spectrophotometer (made in Shanghai of China) in a 3 cm cell.

Standard copper solution, 10.0 mg/L; murexide solution, 2.0 mmol/L; Dissolve 56.8 mg of murexide (from Beijing Reagents, China) in 100 mL of 2% sodium hydroxide. Masking reagent is prepared by mixing solution of 10% sodium fluoride and 10% ammonium citrate in same volume.

Recommended Procedure

Dissolve 0.10 g of sample metal in 10 mL of 50% nitric acid and boil it for evaporating the excess nitric acid. Dilute to 100 mL with distilled water. A known volume of such a solution or waste water containing less than 0.10 mg of copper is taken in a 25 mL standard flask. Then, 2.0 mL of 10% sodium hydroxide, 2 mL of the masking reagent solution and 1.0 mL of murexide solution are added successively. Dilute to required volume with distilled water and mix well. After 2 min, measure absorbances at 480 and 570 nm, respectively, against reagent blank reference.

RESULTS AND DISCUSSION

Absorption Spectra

Figure 1 shows the absorption spectra of murexide, its complexing solution with Cu (II) and its copper chelate at pH 12. From curve C two wavelengths are chosen such that the difference in absorbance is maximal: 480 and 570 nm. β is calculated to be 0.451 from curve A and α is found to be 0.376 from curve B. Therefore, Ac is expressed by following equation[5]:

$$Ac = 1.20(\Delta A - 0.451\Delta A') \qquad (5)$$

Effect of Murexide and Determination of Complexation Ratio

Figure 2 shows the effect of murexide in the presence of the masking reagent on absorbance of murexide at 570 nm against water, that of Cu-murexide solution

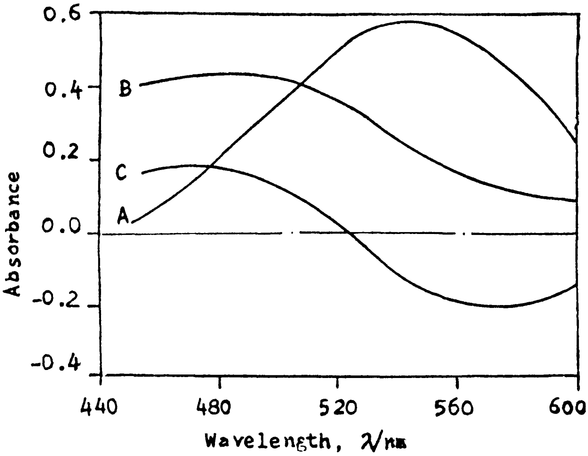

Fig. 1. Absorption spectra of murexide and its Cu(II) chelate: A. murexide, 0.080 mmol/L against water reference; B. the chelate of Cu(II) with murexide against water reference; C, the murexide solution containing 2.00 mg/L of Cu(II).

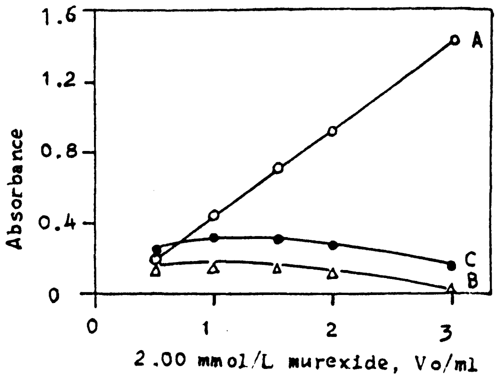

Fig. 2. Effect of murexide at pH 12 in the presence of both fluoride and citrate: A. the reagent blank at 570 nm against water reference; B. the murexide solution containing 2.00 mg/L Cu(II) at 480 nm against the reagent blank reference; C. Ac of chelate formed at 480 nm against water reference.

containing 0.050 mg of Cu at 480 nm against a reagent blank and Ac of chelate formed at 480 nm against water. From curve C the addition of 1 mL of 2.00 mmol/L murexide results in Ac reaching the maximal value. Therefore, 1.0 mL of murexide solution should be selected in all studies. We see from curve B that it is difficult to calculate accurately the complex ratio of Cu to murexide by the mole ratio method[13] because the inflexion is not easy to be found. Because $M_1 = 2.00$ mmol/L and $M_2 = 0.787$ μmol, curves of η and γ against addition of murexide solution (Vo, mL) shown in Figure 3. When V_0 is more than 1.0 mL, γ value remains constant to be 2. Therefore the chelate formed is expressed by Cu (murexide)$_2$. From curve A in Fig. 3, the addition of 1.00 mL of 2.00 mmol/L

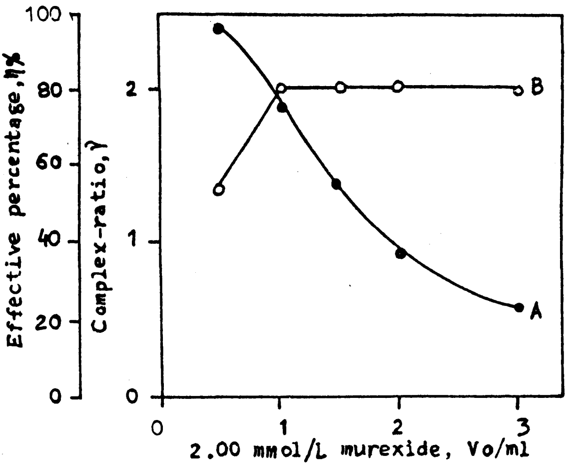

Fig. 3 Curves η and γ against addition of murexide solution (V_0, mL): A. η%; B. γ.

murexide brings out the effective complexation only 75% and it shows the excess of murexide reaches 25% in its 2 mg/L Cu(II) when the reaction is equilibrial. Therefore, it will make serious effect on the determination of trace copper by the single wavelength spectrophotometry.

Effect of Changing Other Conditions

The reaction between Cu(II) and murexide proceeds fairly and rapidly only in basic solution. Therefore, pH 12 is chosen in further study. The formation of chelate Cu $(\text{murexide})_2$ is complete in 1 min. Measurement of absorbances is therefore carried out in 2 min after the addition of murexide, the colour of the complex remainging constant for at least 1 h.

Standard Curve

A series of standard copper solution were prepared and the absorbance of each was measured and plotted. Beer's law was obeyed over the concentration range 0–4.00 mg/L copper. Curves of Ac and ΔA against Cu(II) concentration (x) at 480 nm have been drawn in Fig. 4. We see that in curve A, $Ac = 0.185\ x$ (relative coefficient, $r = 0.9997$) is much more linear than in curve B, $\Delta A = 0.115x$ ($r = 0.904$). Therefore, the accuracy obtained by β-correction method is higher than that by ordinary spectrophotimetric method. The sensitivity of the recommended procedure is increased, as is shown by the higher gradient.

Precision of Method and Detection Limit

Ten replicate determinations of a standard copper solution containing 0.500 mg/L were made, the relative standard deviation (RSD) being 2.5%. However, RSD for the single wavelength method reaches 18%. Therefore, the precision of the mcthod by β-correction spectrophotometry is much better than that by the single wavelength spectrophotometry.

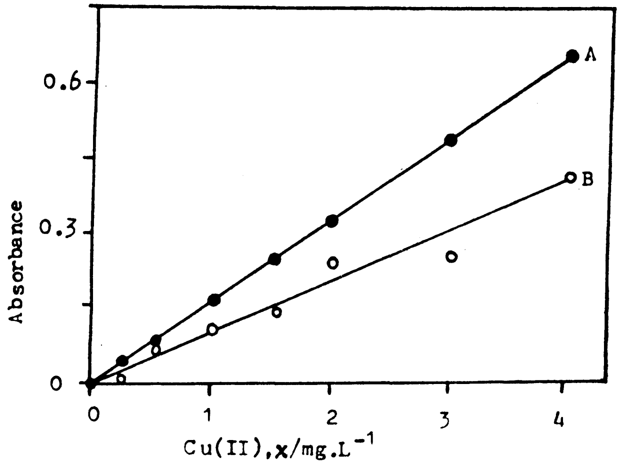

Fig. 4 Standard curves for Cu(II) determination at 480 nm: A. real absorbance, Ac; B. ΔA

We use 0.010 of Ac to calculate the detection limit of copper to be 0.05 mg/L Cu, which is low enough to determine directly copper in metal material and some waste waters.

Effect of Foreign Ions

Once the masking reagent has been added into 50 μg of copper solution, none of the following ions affected direct determination: 10 mg of K^+, Na^+, Cl^-, SO_4^{2-}, F^-, NH_3: 1 mg of Ti^{4+}, Al^{3+}, Fe^{2+}, PO_4^{3-}, Cr^{3+}, Sn^{2+}, Mn^{2+}, Zn^{2+}, Mg^{2+}, Pb^{2+}, Ge^{4+}; 0.1 mg of Hg^{2+}, Ni^{2+}, Cd^{2+}, Ca^{2+}, Co^{2+}. If the concentration of Ca is high, it should be first separated with an oxalate by filtering.

Samples Analysed

As a test of the method copper was determined in two sample metal materials No. 1 and No. 2 and waste water from an electroplating factory (sample No. 3). The results have been listed in Table 1. It was found that the recovery is between 97.4–104% and RSDs is less than 4.4%.

TABLE-1
ANALYTICAL RESULTS OF COPPER IN METAL AND WATER

Sample no.	Copper/mg kg^{-1}		RSD, %	Recovery, %
	Added	Found*		
1	0	365	4.4	
	100	469		104
2	0	998	2.6	
	1000	2010		101
3	0	0.764	1.9	
	1.00	1.938		97.4

*Average of 6 determinations

REFERENCES

1. Ishil Halme , *Anal. Chim. Acta*, **101**, 423 (1978).
2. X.W. He, *Anal. Chim. Acta*, **131**, 195 (1981).
3. T. Odashima, *Anal. Chim. Acta*, **83**, 431 (1976).
4. Dahl, *Anal. Chim. Acta*, **62**, 145 (1972).
5. H. Diehl and J.L. Ellingboe, *Anal. Chem.*, **28**, 882 (1956).
6. H.W. Gao and H.L. Shi, *Spectroscopy*, **9**, 47 (1994)
7. K. Wrobel, B. Kwievinska and B. Godlewka, *Chem. Anal.*, **40**, 631 (1995).
8. G. Asgedom and B.S. Chandravanshi, *Annali di Chimica*, **86**, 485 (1996).
9. K. Matsubara, T. Irie and K. Bekama, *Chem. Pharmaceutical Bull*, **45**, 378 (1997).
10. H.W. Gao, *Water Treat.*, **10**, 367 (1995).
11. ________, *J. Anal. Chem.*, **52**, 141 (1997).
12. S.G. Kawatkar and R.V. Nimbalkar, *J. Indian Chem. Soc.*, **74**, 69 (1997).
13. W. Likussar, *Anal. Chem.*, **45**, 1926 (1973).

(*Received*: 25 April 1997; *Accepted*: 3 September 1997) AJC-1328