

β -Correction Spectrophotometric Investigation of Copper Chelate Solution with Acid Chrome Blue K and Determination of Trace Copper

HONG-WEN GAO*, YUN-SHENG CHEN† and PENG-FEI ZHANG‡

Huaibei Institute of Environment Science

Huaibei, AH 235 000, PR China

The present work reports uses the updated principle named β -correction theory to analyse spectrophotometrically copper chelate solution with acid chrome blue K (ACBK). The complexation ratio and real molar absorptivity (ϵ_r) of chelate formed and effective percentage of ligand ACBK have been worked out easily and acceptably. Using this reaction trace amount of copper has also been determined accurately by β -correction spectrophotometry. The results show that the chelate formed is expressed by Cu(ACBK) at pH 12. Its $\epsilon_r = 1.52 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 580 nm. Beer's law is obeyed over the concentration range 0–2.00 mg/L Cu. The relative standard deviations are less than 3.7% and the recovery of copper between 94–108%.

INTRODUCTION

In the field of spectrophotometric analysis one ligand is often selective to chelate a metal ion but perhaps not sensitive because of the interference of excess ligand in its metal chelate solution. To increase the sensitivity such an interference must be eliminated. One of the methods is to separate the excess ligand using the physical way, but it is usually very complicated and not practical. Because of this elimination, β -correction principle was established in 1994¹ and later it was improved^{2,3}. It applies the calculation formula to work out the real absorbance of chelate formed and gives the effective percentage of ligand in its metal solution. So the effect of excess of ligand is eliminated. This principle has been accepted and used widely^{4–8} for analysis of metal chelates. Here β -correction principle is being used for the spectrophotometric investigation of copper chelate solution.

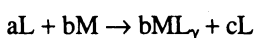
Copper often exists in metal material and in some wastewaters polluted by it, for example, the machine-making, the metallurgical and other industries. Its traditional spectrophotometric determination involves neocuproine⁹ and bathocuproine¹⁰, etc. The reaction between Cu(II) and acid chrome blue K (ACBK) at pH 12 is sensitive. In the past, because of the interference of excess of ACBK, the common spectrophotometry gave very high error in the determina-

†Huaibei Environment Monitoring Centre, Huaibei, AH 235 000, PR China.

‡Department of Chemistry, Huaibei Coal Teachers College, AH 235 000, PR China.

tion of trace amounts of copper. The β -correction method is different from other dual-wavelength methods¹¹⁻¹³. It is the first to eliminate completely the effect of the excess of ligand to achieve the real absorbance of the chelate. The sensitivity, precision and accuracy are all higher than those for the single wavelength method. By means of this principle the complexation ratio of Cu(II) to ACBK has been determined to be 1 : 1 which is easier in operation than one of the other methods, for example, the molar ratio¹⁴, equilibril movement¹⁵, etc. The real molar absorptivity of chelate Cu(ACBK) at 580 nm is determined to be $1.52 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ which is 4 times higher than its apparent molar absorptivity .

The dual-wavelength principle may be illiustrated by the following reaction with example of ligand (L) with metal (M).



where a and b are the molar concentrations of L and M at the beginning, respectively, c is the concentration of excess of L in its M equilibril solution and the term γ is the stoichiometric ratio of L to M. The real absorbance (A_c) of chelate ML_{γ} at wavelength λ_2 should be expressed by

$$A_c = (\Delta A - \beta \cdot \Delta A') / (1 - \alpha \cdot \beta) \quad (1)$$

where ΔA and $\Delta A'$ are the absorbance of the chelated solution against its reagent blank at λ_2 and λ_1 , respectively, and β and α are correction coefficients. They can be expressed by, respectively,

$$\beta = A_0 / A'_0 \quad (2)$$

and

$$\alpha = A'_{\alpha} / A_{\alpha} \quad (3)$$

where A_0 , A'_0 , A_{α} and A'_{α} are absorbances of L solution and ML_{γ} solution (where M concentration is much more than L) against water at λ_2 and λ_1 , respectively.

The effective percentage ($\eta\%$) of L and its M complexation ratio and (γ) may be expressed by equations 4 and 5 respectively.

$$\eta = (A_c - \Delta A) / \beta A'_0 \times 100\% \quad (4)$$

and

$$\gamma = M_1(0.01\eta) / M_2 \quad (5)$$

where M_1 and M_2 are the molar concentrations of L and M respectively at the beginning of reaction.

From ΔA the apparent molar absorptivity (ϵ_a) of the chelate may be calculated; therefore its real molar absorptivity (ϵ_r) should be expressed by

$$\epsilon_r = \frac{A_c}{\delta \cdot c}$$

where c is the molar concentration of ligand in its chelate solution and δ is the thickness (1 cm) of the used cell.

EXPERIMENTAL

Visible spectra were recorded with a Model 722 spectrophotometer (Shanghai 3rd Analytical Instruments, China) in a 1 cm cell.

Standard copper(II) solution, 10.0 mg/L; ACBK solution, 2.00 mmol/L: dissolve 0.117 g of ACBK (Shanghai Reagents) in 100 mL of 5% sodium hydroxide. Hydrogen peroxide solution, 2% (A.R., Shanghai Reagents); ascorbic acid solution, 3% (A.R., Shanghai Chemicals); ammonium chloride solution, 20% (A.R., Shanghai Chemicals); diantipyrylmethane solution, 2%: dissolve 2 g of diantipyrylmethane (C.P., Beijing Chemicals, China) in 100 mL of 2 mol/L hydrochloric acid. Ammonia solution, 1 mol/L (A.R., Bengbu Chemicals, China); chloroform (A.R., Huainan Chemicals).

Recommended Procedures

To an aliquot of a solution containing less than 50 µg of copper, add 8 mL of concentrated hydrochloric acid, 10 mL of ammonium chloride solution and 5 mL of ascorbic acid solution. Dilute to about 100 mL then add 2 mL of diantipyrylmethane solution and mix. The solution is transferred into a separating funnel and 20 mL of chloroform added. After separating the aqueous layer, the metal ions Cu(I) are stripped with two 5 mL portion of ammonia solution. The final aqueous layer is taken in a 25 mL volumetric flask. Then, add 2 mL hydrogen peroxide solution to change Cu(I) into Cu(II), 2 mL of 10% sodium hydroxide and 0.50 mL of ACBK solution. Dilute to standard volume and mix well. After 20 min, measure the absorbances at 470 and 580 nm, respectively, against reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra: The absorption spectra of ACBK and its copper chelate solution have been drawn in Figure 1. Curve 2 shows the spectra of copper chelate with ACBK which is measured from the solution adding at beginning 0.20 mmol/L Cu and only 0.01 mmol/L ACBK (ACBK is believed to chelate Cu(II) completely because of the strong excess of Cu(II) against water. From curve 3, two wavelengths should be selected, at the valley, 470 nm and at the peak, 580 nm, for obtaining the maximal sensitivity. From curve 1, β has been calculated to be 3.54 and from curve 2, α only 0.02. Hence $\alpha \cdot \beta = 0.07$ and it is much less than 1. Therefore, A_c and η expressions are simplified as

$$A_c = \Delta A - 3.54\Delta A'$$

and

$$\eta = -\frac{\Delta A'}{A'_0}$$

Effect of ACBK Concentration Change: Figure 2 shows the effect of ACBK concentration. From curve 2 because the inflexion point can be found with difficulty, the molar ratio method will bring out inaccurate complex-ratio result. Both η and γ are computed from curves 1 and 3 in Figure 2 and the above equations. Their curves have been drawn in Figure 3. From curve 2 we see that

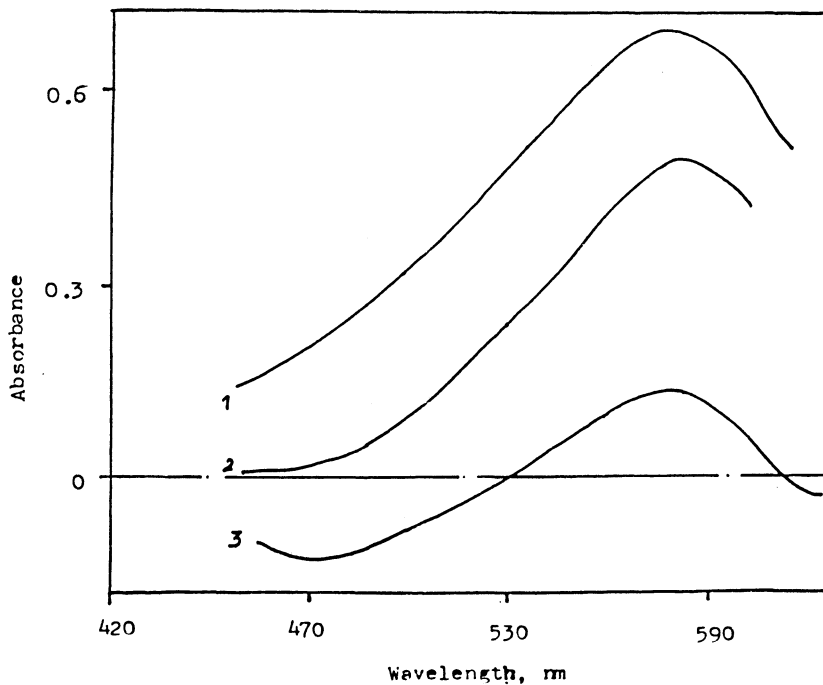


Fig. 1. Absorption spectra of ACBK and its copper(II) chelate solution at pH 12: 1, 0.040 mmol/L ACBK against water; 2, chelate Cu(ACBK) against water; 3, 2.0 mg/L Cu(II) + 0.040 mmol/L ACBK against reagent blank.

when the addition (V_0) of ACBK solution is more than 0.5 mL, γ value reaches maximal and remains constant to be 1. Therefore, the complexation ratio, Cu: ACBK = 1 : 1. The chelate formed is expressed by Cu(ACBK). From curve 2, at the working beginning concentration 2.00 mmol/L ACBK, $\eta = 75\%$. It shows that the excess of ACBK owns 25% in 2.00 mg/L Cu(II) and it is believed to affect certainly the measurement of the chelate's absorbance.

Effect of Changing Other Conditions: The reaction between Cu(II) and ACBK can proceed rapidly in alkaline solution. At such a pH 12, copper hydroxide has not been found to be formed when Cu concentration is lower than 0.2 mmol/L. The formation of chelate Cu(ACBK) is complete in 20 min. Measurement of the absorbance was therefore carried out in 20 min after the addition of ACBK.

Calibration Graph: A series of standard copper solutions were prepared and the absorbance of each was measured and plotted. Beer's law was obeyed over the concentration range 0–2.0 mg/L copper. Curves Ac and ΔA against Cu concentration (x mg/L) have been drawn in Figure 4. We find that curve 1 is more linear than curve 2. It shows that the accuracy by the β -correction spectrophotometry is higher than that for the single wavelength method. The real molar absorptivity (ϵ_r) at 580 nm can be calculated to be 1.52×10^4 L mol⁻¹ cm⁻¹ from curve 1 but from curve 2 it is apparent that ϵ_a is only 0.42×10^4 .

Effect of Foreign Ions: Once the recommended pretreatment is carried out none of the following ions affect the measurement the determination of 2 mg/L Cu(II); 100 mg/L K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} ; 10 mg/L Fe^{3+} , Cr^{3+} , Co^{2+} , Mn^{2+} , Zn^{2+} , Ce^{4+} , V^{5+} , Se^{2+} , La^{3+} , Zr^{3+} , Ni^{2+} , Ti^{4+} and 2 mg/L Cd^{2+} , Hg^{2+} , Pb^{2+} .

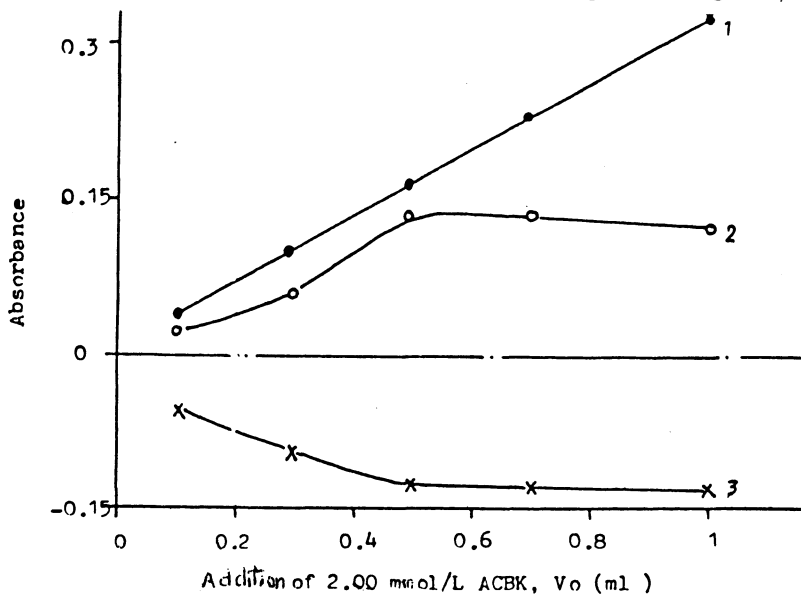


Fig. 2. Effect of ACBK concentration at pH 12 : 1, reagent blank at 470 nm against water ($\Delta\circ'$); 2, 2.00 mg/L Cu(II) + ACBK at 580 nm against reagent blank ($\Delta\Delta$); 3, same as 2 at 470 nm ($\Delta\Delta'$)

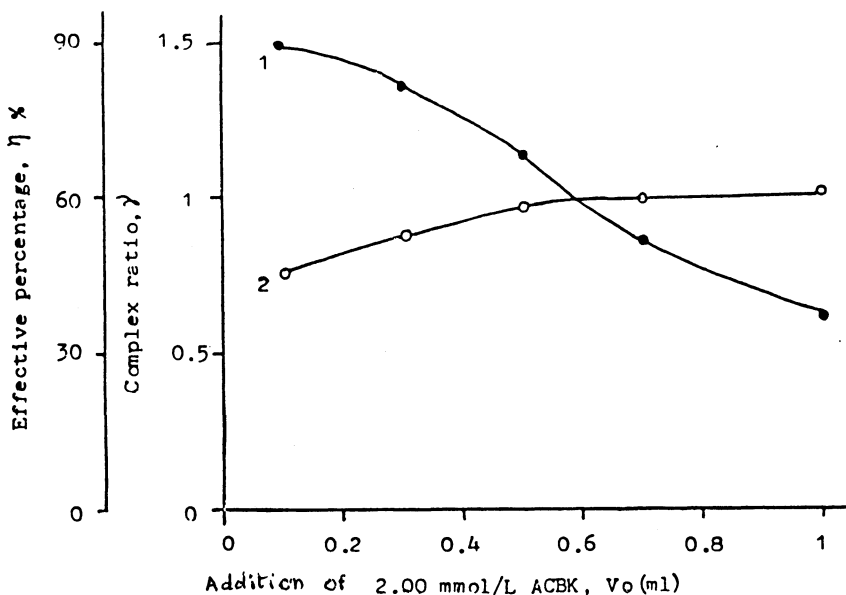


Fig. 3. Curves η and γ against: 1, $n\%$; 2, γ

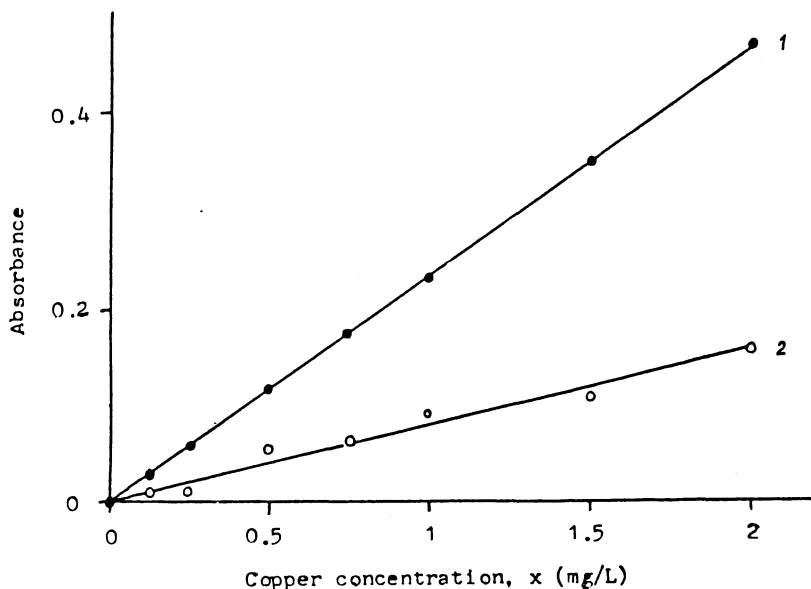


Fig. 4. Standard curves at 580 nm: 1, $Ac(x)$; 2, $\Delta\Delta(x)$

Precision and Detection Limit: For ten replicate determinations of a standard solution containing 0.20 mg/L Cu(II), the relative standard deviation (RSD) was 2.1%. However, the RSD for the single wavelength spectrophotometry is equal to 11%. The precision for the β -correction method is therefore higher than that of the ordinary spectrophotometry.

The detection limit of copper was equal to 0.04 mg/L for 0.010 of Ac . Therefore, the minimum detection concentration can reach to 0.01 mg/L Cu(II) because of the preconcentration of copper in the recommended procedure.

Table-1
Determination of copper in some samples

S. No.	Copper (mg/kg)		RSD, %	Recovery, %
	Added	Found*		
1.	0	7.12	1.6	108
	10.0	17.9		
2.	0	0.120	3.7	95
	0.10	0.215		
3.	0	776	3.1	94
	500	1246		
4.	0	299	3.6	102
	300	605		

*Average of 6 determinations

Samples Analysed: As a test of the method copper was determined in some samples, for example, electroplating wastewater (1), river water (2), steelmaterial (3) and ore (4). The results are listed in Table-1. We see the relative standard deviations are less than 3.7% and the recovery of copper between 94 and 108%.

REFERENCES

1. H.W. Gao and P.F. Zhang, *Analyst*, **119**, 2109 (1994).
2. H.W. Gao, *Talanta*, **42**, 891 (1995).
3. _____ *Anal. Proc.*, **32**, 479 (1995).
4. A.M. Dietrich, *Wat. Env. Res.*, **67**, 391 (1995).
5. G.H. Lu, *Food Chem.*, **50**, 91 (1994).
6. K. Wrobel, B.K. Wicinska and B. Godlewska, *Chem. Anal.*, **40**, 631 (1995).
7. S.P. Arya and M. Mahajan, *J. Indian Chem. Soc.*, **74**, 66 (1997).
8. P.F. Zhang, H.W. Gao and G.W. Cui, *Can. J. Appl. Spectrosc.*, **41**, 1 (1996).
9. A.J. Erank, A.B. Goulston and A.A. Deacutis, *Anal. Chem.*, **29**, 750 (1975).
10. D. Blair and H. Diehl, *Talanta*, **7**, 163 (1961).
11. H.W. Gao *Huanjing Kexue*, **2**, 82 (1993).
12. K.L. Ratzlaff, *Anal. Chem.*, **49**, 2170 (1977).
13. H. Wananabe and H. Ohmori, *Talanta*, **26**, 959 (1979).
14. N. Zhou, *Analyst*, **118**, 1077 (1993).
15. H.E. Beut, *J. Am. Chem. Soc.*, **64**, 568 (1941).

(Received: 24 February 1998; Accepted: 3 November 1998)

AJC-1615