

# Stability Constants of Cobalt(II) and Copper(II) Complexes with 3-[(*o*-Carboxy-*p*-nitrobenzene)azo]chromotropic Acid and Selective Determination of Copper(II) by Competition Coordination

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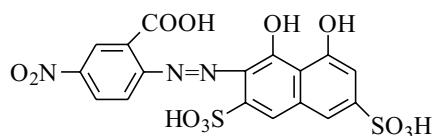
*Key words*

- competition coordination for selective determination
- spectral correction technique
- determination of copper(II)
  - stability constants
  - 3-[(*o*-carboxy-*p*-nitrobenzene)azo]chromotropic acid

A method for selective determination of copper(II) based on the reactions of copper(II) or cobalt(II) with 3-[(*o*-carboxy-*p*-nitrobenzene)azo]chromotropic acid (CNBAC) at pH = 11.4 was developed. Results have shown that two complexes, Co(CNBAC)<sub>2</sub> and Cu(CNBAC), were formed, whose cumulative stability constants were  $5.22 \times 10^9$  and  $7.61 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ , respectively, and their molar absorption coefficients were  $1.19 \times 10^4$  and  $2.12 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 610 nm. The competition coordination of Cu<sup>II</sup> and Co<sup>II</sup> with CNBAC was applied for selective determination of Cu<sup>II</sup> by the spectral correction technique. In the absence of any masking reagent, the recommended method was selective and was applied for quantitative determination of copper(II) in river and waste water samples.

## INTRODUCTION

Copper often exists in wastewater, ore, metal material, and so on. Chromogenic reagents, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol,<sup>1</sup> dithizone, di(2-pyridylmethanone)-2-(5-nitropyridyl) hydrazone,<sup>2</sup> monoethyl- $\alpha$ -anilinobenzylphosphonate,<sup>3</sup> bidentate pyridylazo compounds,<sup>4</sup> 2-nitroso-1-naphtholsulfonic acid<sup>5</sup> and others<sup>6–8</sup> were applied to the determination of copper(II) by spectrophotometry. Synthesis of the novel ligand, 3-[(*o*-carboxy-*p*-nitrobenzene)azo]chromotropic acid (CNBAC), was performed and its structural formula is given below.



CNBAC forms complexes with many metal ions such as Ni<sup>II</sup>, Cd<sup>II</sup>, Zn<sup>II</sup>, Pb<sup>II</sup> and alkaline earths(II). Therefore, its selectivity is poor in the detection application. Selective detection of a metal was not possible unless several masking reagents were used simultaneously. Recently, the competition coordination for selective determination (CCSD) was developed<sup>9</sup> using a metal to substitute for another metal from the complex. Thus, the first metal must have a much stronger complexation with the ligand than other metals. We found that copper(II) has the strongest complexation with CNBAC of most metals at pH = 11.4. Therefore, Cu<sup>II</sup> may substitute for many metals from their CNBAC complexes. In the present work, Co<sup>II</sup> was selected because of its sensitive reaction with CNBAC. The CCSD process of Cu<sup>II</sup> is described simply as follows: enough Co<sup>II</sup> is added into a CNBAC solution to bind complete CNBAC and then a

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trace amount of  $\text{Cu}^{\text{II}}$  is added into the mixture to substitute for the  $\text{Co}^{\text{II}}$  from only the Co-CNAC complex to form the Cu-CNAC complex. The substitution reaction between  $\text{Cu}^{\text{II}}$  and Co-CNAC complex at  $\text{pH} = 11.4$  was investigated in detail by a spectral correction technique<sup>10</sup> instead of standard spectrophotometry. The method is selective without the use of masking reagents because of the excessive amount of  $\text{Co}^{\text{II}}$ . The spectral correction technique enabled easier determination of the complex ligand to metal ratio, stability constant and molar absorption coefficient than classical methods, *e.g.*, the mole ratio,<sup>11</sup> continuous variations,<sup>12</sup> and equilibrium shift methods.<sup>13</sup> Determination of the trace amount of  $\text{Cu}^{\text{II}}$  in water samples was performed.

## EXPERIMENTAL

### Apparatus and Reagents

The absorption spectra were recorded with a TU1901 spectrophotometer (PGeneral, Beijing) and the independent absorbance of solution was measured with a Model 722 (Shanghai 2nd Instruments), both with 1.0-cm cells. A conductivity meter Model DDS-11A (Tianjin Second Analytical Instruments) was used to measure the conductivity together with a Model DJS-1 conductivity immersion electrode (electrode constant 0.98) (Shanghai Tienkuang Devices) in the production of deionized water of  $0.5\text{--}1\ \mu\Omega^{-1}\ \text{cm}^{-1}$ . The solution pH was measured on a pH-2C acidity meter (Leici Instruments, Shanghai, China) and a Model 620D pH Pen (Shanghai Ren's Electronic).

Standard  $\text{Co}^{\text{II}}$  ( $1.000\ \text{g}\ \text{dm}^{-3}$ ) and  $\text{Cu}^{\text{II}}$  ( $1.000\ \text{g}\ \text{dm}^{-3}$ ) solutions were prepared by dissolving 1.000 g of high-purity metals in hydrochloric and nitric acids and then diluted to  $1000\ \text{cm}^3$  with deionized water. Standard solutions of  $\text{Co}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$ , both  $10.0\ \text{mg}\ \text{dm}^{-3}$ , must be prepared daily. CNAC ( $1.20\ \text{mmol}\ \text{dm}^{-3}$ ) solution was prepared by dissolving 0.3200 g of 3-[(*o*-carboxy-*p*-nitrobenzene)azo]chromotropic acid ( $w(\text{CNAC}) > 98\%$ ) in  $500\ \text{cm}^3$  of deionized water. It should be stored in a dark bottle and at  $T < 5\ ^\circ\text{C}$ . The Co-CNAC complex solution was prepared by mixing  $10\ \text{cm}^3$  of the hydrated cobalt chloride (A. R., Shanghai Reagents) solution (1.5 %) prepared in deionized water with  $50.0\ \text{cm}^3$  of  $1.20\ \text{mmol}\ \text{dm}^{-3}$  CNAC and  $10\ \text{cm}^3$  of buffer solution,  $\text{pH} = 11.4$ , and then diluting it to  $100\ \text{cm}^3$  with deionized water. The novel chromogenic reagent contained  $0.600\ \text{mmol}\ \text{dm}^{-3}$  Co(CNAC) complex (1:1) because  $\text{Co}^{\text{II}}$  concentration is more than 10 times that of CNAC where the free CNAC approaches zero. The buffer solution,  $\text{pH} = 11.4$ , was prepared with disodium hydrogen phosphate (A. R., Shanghai Chemicals) and NaOH.

### Methods

*Determination of Stability Constants of  $\text{Co}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  Complexes with CNAC.* – Into a  $25\ \text{cm}^3$  calibrated flask,  $10.0\ \mu\text{g}$  of  $\text{Co}^{\text{II}}$  or  $\text{Cu}^{\text{II}}$ ,  $2.5\ \text{cm}^3$  of buffer solution and  $1.00\ \text{cm}^3$  of  $1.20\ \text{mmol}\ \text{dm}^{-3}$  CNAC were added. The mixture was di-

luted to  $25\ \text{cm}^3$  with deionized water and thoroughly mixed. Thus, the final mass concentration,  $\gamma$ , of  $\text{Cu}^{\text{II}}$  (or  $\text{Co}^{\text{II}}$ ) in the sample was  $0.4\ \mu\text{g}\ \text{cm}^{-3}$  and the mole concentration of CNAC was  $0.048\ \mu\text{mol}\ \text{cm}^{-3}$ . After 10 min, the absorbances were measured at 525 and 610 nm against the blank treated in the same way without  $\text{Co}^{\text{II}}$  or  $\text{Cu}^{\text{II}}$ . Finally, the real absorbance ( $A_c$ ) of the complexes was calculated by the relation:<sup>14–15</sup>

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha \beta} \quad \text{where} \quad (1)$$

$$\alpha = \frac{\varepsilon^{\lambda_1}(\text{ML}_n)}{\varepsilon^{\lambda_2}(\text{ML}_n)} \quad \text{and} \quad \beta = \frac{\varepsilon^{\lambda_2}(\text{L})}{\varepsilon^{\lambda_1}(\text{L})}$$

Here, symbols  $\Delta A$  and  $\Delta A'$  are the absorbances of the M-L (metal-ligand) solution against the L solution without M, measured at the peak wavelengths ( $\lambda_2$ ) and the valley wavelength ( $\lambda_1$ ). The correction coefficients  $\alpha$  and  $\beta$  are constants. The symbols  $\varepsilon^{\lambda_1}(\text{ML}_n)$ ,  $\varepsilon^{\lambda_2}(\text{ML}_n)$ ,  $\varepsilon^{\lambda_1}(\text{L})$  and  $\varepsilon^{\lambda_2}(\text{L})$  are the molar absorption coefficients of the complex (ML) solution without free L and the L solution without M against water reference, measured at  $\lambda_1$  and  $\lambda_2$ .

The fraction of the effective CNAC,  $x(\text{CNAC})_{\text{eff}}$  and the mole ratio of CNAC to  $\text{Co}^{\text{II}}$  or  $\text{Cu}^{\text{II}}$ ,  $r(\text{CNAC}, \text{Co}^{\text{II}})$  and  $r(\text{CNAC}, \text{Cu}^{\text{II}})$ , were calculated according to Eq (2).

$$x = \frac{A_c - \Delta A}{A_0} \quad \text{and} \quad r = x \frac{c(\text{L})}{c(\text{M})} \quad (2)$$

The symbols  $c(\text{M})$  and  $c(\text{L})$  denote the initial concentration of  $\text{Co}^{\text{II}}$  or  $\text{Cu}^{\text{II}}$  and CNAC, respectively.  $A_0$  is the absorbance of CNAC solution against water at 610 nm (*cf.* Figure 1).

*Determination of  $\text{Cu}^{\text{II}}$  in Water.* – A known volume of a sample containing less than  $25.0\ \mu\text{g}$  of  $\text{Cu}^{\text{II}}$  was put into a  $25\ \text{cm}^3$  volumetric flask.  $2.5\ \text{cm}^3$  of  $\text{pH} = 11.4$  buffer solution and  $3.0\ \text{cm}^3$  of the Co-CNAC complex ( $0.600\ \text{mmol}\ \text{dm}^{-3}$ ) were added, diluted to  $25\ \text{cm}^3$  with deionized water and mixed well. After 20 min, the absorbances were measured at 525 and 610 nm against a reagent blank without  $\text{Cu}^{\text{II}}$ .

## RESULTS AND DISCUSSION

### Absorption Spectra and Analysis

Figure 1 shows the absorption spectra of the CNAC, Co-CNAC, Cu-CNAC and Cu-Co-CNAC solutions at  $\text{pH} = 11.4$ . From curve 1, it is seen that the absorption maximum of CNAC is located at 550 nm. Similarly, curve 2 and 3 show that the maximum of the Co-CNAC complex is located at 550 nm and that of the Cu-CNAC complex at 610 nm. Spectra 4 and 5 show that both the Co-CNAC and Cu-CNAC solutions have the maximum at 610 nm and the valley at 550 nm. Hence, such two wavelengths were selected in studying the complexing of

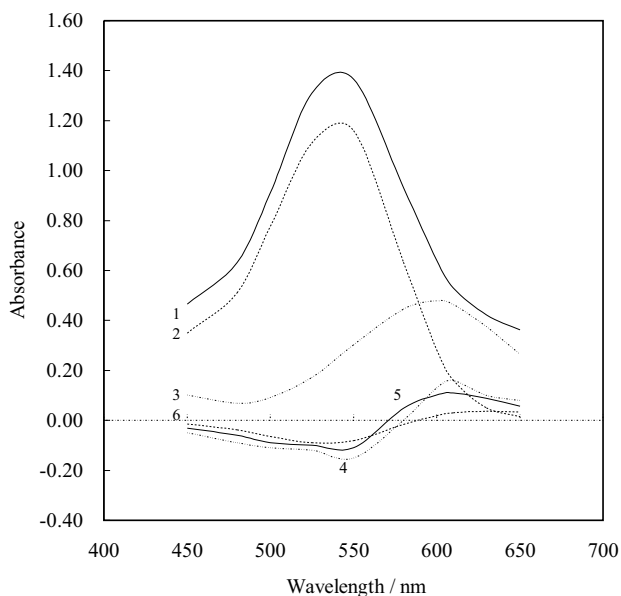


Figure 1. Absorption spectra of CNBAC and its  $\text{Co}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  complex solutions at  $\text{pH}=11.4$ : 1) CNBAC ( $0.048 \mu\text{mol cm}^{-3}$ ) solution; 2)  $\text{Co}$  ( $0.400 \mu\text{mol cm}^{-3}$ ) – CNBAC ( $0.096 \mu\text{mol cm}^{-3}$ ) complex solution (no longer containing free CNBAC), and 3)  $\text{Cu}$  ( $0.120 \mu\text{mol cm}^{-3}$ ) – CNBAC ( $0.024 \mu\text{mol cm}^{-3}$ ) complex solution (no longer containing free CNBAC); 4)  $\text{Co}$  ( $0.400 \mu\text{g cm}^{-3}$ ) – CNBAC ( $0.048 \mu\text{mol cm}^{-3}$ ) solution; 5)  $\text{Cu}$  ( $0.400 \mu\text{g cm}^{-3}$ ) – CNBAC ( $0.048 \mu\text{mol cm}^{-3}$ ) solution; 6)  $\text{Cu}$  ( $0.800 \mu\text{g cm}^{-3}$ ) –  $\text{Co}$ (CNBAC) ( $0.048 \mu\text{mol cm}^{-3}$ ) solution. 1, 2 and 3 against water reference and the other against the reagent blank without  $\text{Co}^{\text{II}}$  and/or  $\text{Cu}^{\text{II}}$ .

$\text{Co}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  with CNBAC. The correction constants were calculated to be  $\beta(\text{L})_{610/525} = 0.145$  from curve 1,  $\alpha(\text{CoL})_{525/610} = 2.46$  from curve 2, and  $\alpha(\text{CuL})_{525/610} = 0.371$  from curve 3. The following relations were used to calculate the real absorbance of the Co-CNABAC and Cu-CNABAC complexes at 610 nm:  $A_c(\text{Co-CNABAC}) = 1.56(\Delta A - 0.145 \Delta A')$  and  $A_c(\text{Cu-CNABAC}) = 1.06(\Delta A - 0.145 \Delta A')$ .

Curve 6 in Figure 1 shows that the maximum of the Cu-Co-CNABAC solution is located at 610 nm and the valley at 525 nm. The two wavelengths were used in studying the quantitative determination of  $\text{Cu}^{\text{II}}$ .  $\beta(\text{CoL})_{610/525} = 1/\alpha(\text{CoL})_{525/610} = 0.407$  from curve 2 and  $\alpha(\text{CuL})_{525/610} = 0.371$  from curve 3. The following expression was used to calculate the real absorbance of the Cu-CNABAC complex formed in the substitution reaction:  $A_c = 1.18(\Delta A - 0.407\Delta A')$ .

#### Effect of pH on the Formation of $\text{Co}^{\text{II}}$ and $\text{Cu}^{\text{II}}$ Complexes with CNBAC

The effect of pH on the formation of  $\text{Co}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  complexes with CNBAC is shown in Figure 2. We observed that the ligand to metal ratio ( $r$ ) in the Cu-CNABAC complex remained almost constant when  $\text{pH} > 10.4$ . In this work, a  $\text{pH} = 11.4$  buffer solution was used. We observed that other metals can also form a similar violet complex

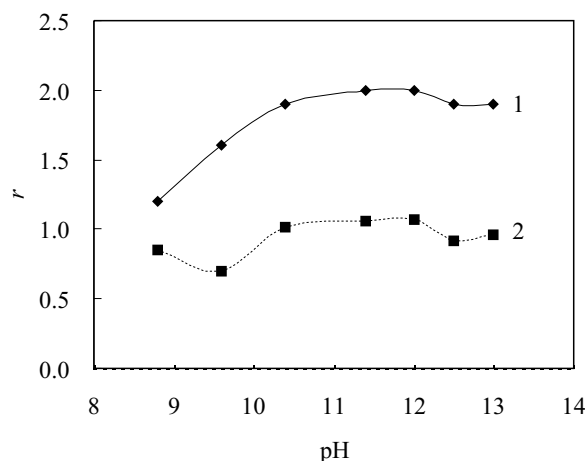


Figure 2. Effect of pH on the ratio ( $r$ ) of CNBAC to  $\text{Co}^{\text{II}}$  and CNBAC to  $\text{Cu}^{\text{II}}$ : 1) solution containing  $0.048 \mu\text{mol cm}^{-3}$  CNBAC and  $0.400 \mu\text{g cm}^{-3}$   $\text{Cu}^{\text{II}}$ , and 2) solution containing  $0.048 \mu\text{mol cm}^{-3}$  CNBAC and  $0.400 \mu\text{g cm}^{-3}$   $\text{Co}^{\text{II}}$ .

at  $\text{pH} = 11.4$ , e.g.,  $\text{Ni}^{\text{II}}$ ,  $\text{Pb}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$ ,  $\text{Ca}^{\text{II}}$  and  $\text{Mg}^{\text{II}}$ . However, all of these will not react with CNBAC because no free CNBAC exists in the presence of plenty of  $\text{Co}^{\text{II}}$ .

#### Determination of Stability Constants of $\text{Co}^{\text{II}}$ and $\text{Cu}^{\text{II}}$ Complexes with CNBAC

By varying the addition of  $1.20 \text{ mmol dm}^{-3}$  CNBAC, the absorbances of the Cu-CNABAC and Co-CNABAC solutions were measured.

The variation of  $r$  is shown in Figure 3. From curve 1, it follows that  $r$  approaches a maximum at 2 in the Co-CNABAC system when more than  $1.8 \mu\text{mol}$  CNBAC (i.e. more than  $1.5 \text{ cm}^3$  of  $1.20 \text{ mmol dm}^{-3}$  CNBAC) was added into  $25 \text{ cm}^3$  of sample solution containing  $0.400 \mu\text{g cm}^{-3}$  of  $\text{Co}^{\text{II}}$ . Similarly, curve 2 shows that  $r$  approaches a maximum at 1 in the Cu-CNABAC system when more than  $1.20 \mu\text{mol}$  CNBAC ( $>1.0 \text{ cm}^3$  of  $1.20$

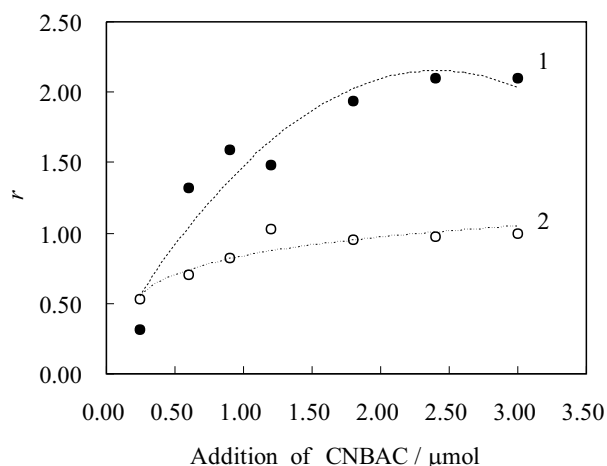


Figure 3. Effect of addition of the CNBAC solution on the ratio,  $r(\text{CNBAC}, \text{Co}^{\text{II}})$  and  $r(\text{CNBAC}, \text{Cu}^{\text{II}})$ : 1) solution containing  $0.400 \mu\text{g cm}^{-3}$   $\text{Co}^{\text{II}}$ , and 2) solution containing  $0.400 \mu\text{g cm}^{-3}$   $\text{Cu}^{\text{II}}$ .

TABLE I. Determination of the stability constant and the molar absorption coefficient of complexes  $\text{Co}(\text{CNBAC})_2$  and  $\text{Cu}(\text{CNBAC})$  at pH = 11.4 and 25 °C, at an ionic strength of 0.025 mol dm<sup>-3</sup>

$n^{(a)}$	$K_n / \text{dm}^3 \text{ mol}^{-1}$	$\varepsilon_r^{(b)} / \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
$\text{Co}(\text{CNBAC})_2$		
1 <sup>st</sup>	$9.24 \times 10^4$	$6.04 \times 10^3$
2 <sup>nd</sup>	$5.65 \times 10^4$	$1.19 \times 10^4$
$\text{Cu}(\text{CNBAC})$		
1 <sup>st</sup>	$7.61 \times 10^5$	$2.12 \times 10^4$

(a) Step number. (b) At 610 nm.

mmol dm<sup>-3</sup> CNBAC) was added. Thus, the complexes  $\text{Co}(\text{CNBAC})_2$  and  $\text{Cu}(\text{CNBAC})$  were formed.

The stepwise stability constant ( $K_n$ ), cumulative constant ( $K$ ) and stepwise molar absorption coefficient ( $\varepsilon$ ) of M-L complex can be calculated by means of expressions:<sup>15</sup>

$$K_n = \frac{r+1-n}{(n-r)(c(\text{L})-rc(\text{M}))} \quad \text{and} \quad K = \prod_{n=1}^r K_n$$

$$\varepsilon^{\lambda_2}(\text{ML}_n) = \frac{A_c}{lc(\text{M})(r+1-n)} - \frac{n-r}{r+1-n} \varepsilon^{\lambda_2}(\text{ML}_{n-1})$$

Symbol  $n$  denotes the step number of the complex and  $l$  is the absorbing path length of the absorption cell.  $r$  is between  $n-1$  and  $n$ . In order to determine the molar absorption coefficients and stability constants of the Co-CNBAAC and Cu-CNBAAC complexes, three solutions were prepared: the first containing 0.400  $\mu\text{g cm}^{-3}$  Co<sup>II</sup> and 0.080  $\mu\text{mol cm}^{-3}$  CNBAC, the second containing 0.400  $\mu\text{g cm}^{-3}$  Co<sup>II</sup> and 0.040  $\mu\text{mol cm}^{-3}$  CNBAC, and the third containing 0.400  $\mu\text{g cm}^{-3}$  Cu<sup>II</sup> and 0.080  $\mu\text{mol cm}^{-3}$  CNBAC. Four replicated determinations of each were made. The stepwise molar absorption coefficients and stability constants of both the Co-CNBAAC and Cu-CNBAAC complexes are given in Table I. The cumulative stability constants of  $\text{Co}(\text{CNBAC})_2$  and  $\text{Cu}(\text{CNBAC})$  are  $5.22 \times 10^9$  and  $7.61 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$  respectively, at an ionic strength of 0.025 mol dm<sup>-3</sup> at 25 °C. Table I shows that the 1<sup>st</sup>-step stability constant of  $\text{Co}(\text{CNBAC})_2$  was much less than that of  $\text{Cu}(\text{CNBAC})$ . Therefore, trace amounts of Cu<sup>II</sup> can substitute for the Co<sup>II</sup> only from the  $\text{Co}(\text{CNBAC})$  complex to form the  $\text{Cu}(\text{CNBAC})$  complex. This substitution reaction was applied to the determination of trace amounts of Cu<sup>II</sup> with high selectivity.

#### Effect of Addition of Co-CNBAAC Complex on the Formation of Cu-CNBAAC Complex

By varying the addition of 0.600 mmol dm<sup>-3</sup>  $\text{Co}(\text{CNBAC})$ , the absorbances of the Cu-Co( $\text{CNBAC}$ ) solutions were measured at 610 and 525 nm and their curves are shown in

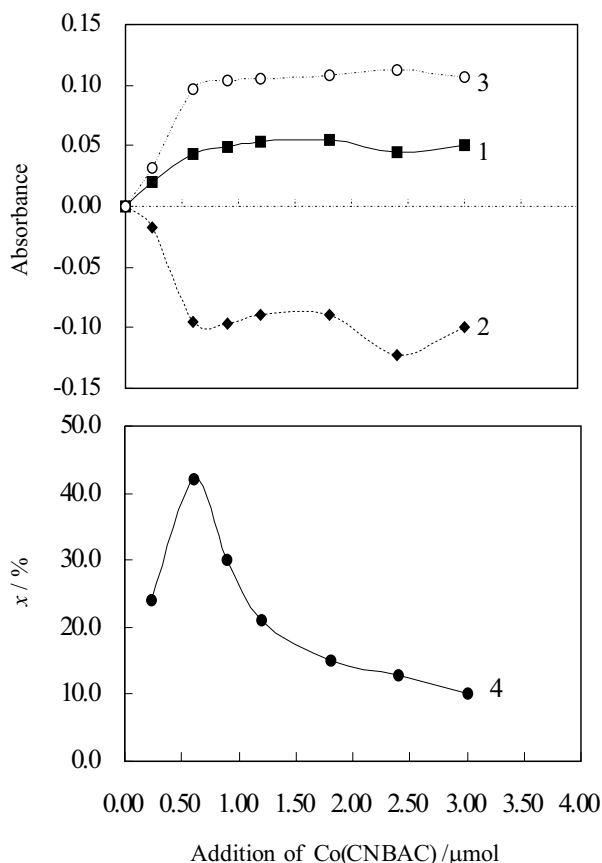


Figure 4. Effect of addition of the  $\text{Co}(\text{CNBAC})$  complex solution on: 1) absorbance of the solution containing 0.400  $\mu\text{g cm}^{-3}$  Cu<sup>II</sup>, measured at 610 nm, and 2) measured at 525 nm, 3)  $A_c$  calculated, 4) effective fraction ( $x / \%$ ) of the  $\text{Co}(\text{CNBAC})$  complex.

Figure 4. Curve 3 approaches a maximum when more than 2.0 cm<sup>3</sup> of 0.600 mmol dm<sup>-3</sup>  $\text{Co}(\text{CNBAC})$  (>1.2  $\mu\text{mol Co}(\text{CNBAC})$ ) was added. So, 3.0 cm<sup>3</sup> of 0.600 mmol dm<sup>-3</sup>  $\text{Co}(\text{CNBAC})$  was used in the quantitative determination of Cu<sup>II</sup>. The effect of  $\text{Co}(\text{CNBAC})$  addition on  $x$  is also shown in Figure 4, curve 4, where the mixture contained 0.400  $\mu\text{g cm}^{-3}$  Cu<sup>II</sup>. We observed that  $x$  was only 15 % when 3.0 cm<sup>3</sup> of 0.600 mmol dm<sup>-3</sup>  $\text{Co}(\text{CNBAC})$  was added. Thus, 85 % of the  $\text{Co}(\text{CNBAC})$  complex added was not substituted by Cu<sup>II</sup>. It is indubitable that such excessive amount of  $\text{Co}(\text{CNBAC})$  severely affected the measurement of the real absorbance of the Cu-CNBAAC complex. Therefore, standard spectrophotometry is inapplicable to the CCSD of a metal. In contrast, the spectral correction technique can provide an accurate trace detection.

#### Time of Formation of Cu-CNBAAC Complex

Figure 5 shows that the substitution of Co<sup>II</sup> from  $\text{Co}(\text{CNBAC})$  with Cu<sup>II</sup> at 25 °C reached equilibrium in 20 min. Initial solution contained 0.400  $\mu\text{g cm}^{-3}$  Cu<sup>II</sup> and 0.072  $\mu\text{mol cm}^{-3}$   $\text{Co}(\text{CNBAC})$ . We observed that the substitution of Co<sup>II</sup> from  $\text{Co}(\text{CNBAC})$  complex with Cu<sup>II</sup> was slower than the direct reaction of Cu with CNBAC.

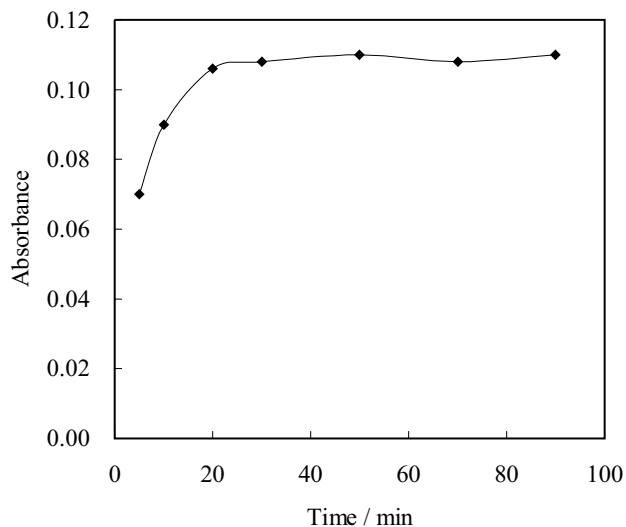


Figure 5. Dependence of the real absorbance ( $A_c$ ) of the Cu-CNAC complex ( $\text{pH} = 11.4$ ,  $T = 25^\circ\text{C}$ ) on the substitution reaction time.

### CCSD of Copper(II)

**Calibration Graph, Precision and Detection Limit.** – A series of standard solutions containing less than  $1.20 \mu\text{g cm}^{-3}$   $\text{Cu}^{\text{II}}$  were prepared and the absorbance of each solution was measured. The results are shown in Figure 6. We can observe that the calculation data (line 2) is much more linear between 0 and  $1.00 \mu\text{g cm}^{-3}$   $\text{Cu}^{\text{II}}$  than the measurement data (line 1), and the slope of line 2 is more than that of line 1. Therefore, the spectral correction technique regularly renders a better accuracy and a higher sensitivity than those obtained in standard spectrophotometry. The regression equation of line 2 is:  $A_c = 0.199x + 0.009$ .

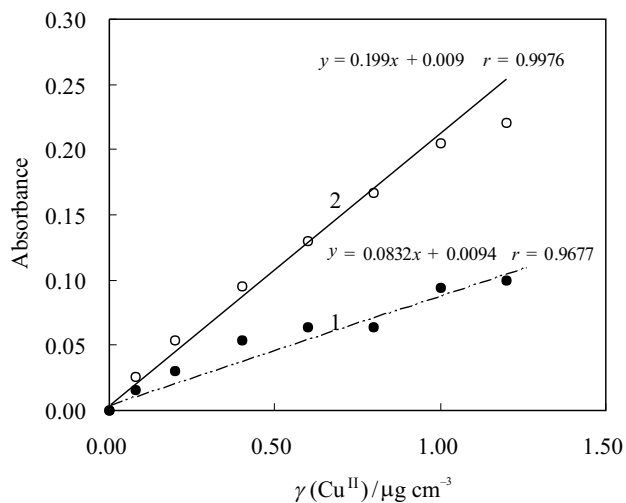


Figure 6. Standard curves for the determination of  $\text{Cu}^{\text{II}}$  using the substitution reaction between  $\text{Cu}^{\text{II}}$  and  $\text{Co}(\text{CNBAC})_2$  at  $\text{pH} = 11.4$ : 1)  $\Delta A$  and 2)  $A_c$ , both at  $610 \text{ nm}$ .

Ten replicate determinations of two standard solutions containing  $0.080$  and  $0.400 \mu\text{g cm}^{-3}$   $\text{Cu}^{\text{II}}$  were carried out. The relative standard deviations (RSDs) were  $3.4$  and  $2.2\%$ , respectively. However, the RSDs were over  $12\%$  in standard spectrophotometry. The conventional formula  $L_{\text{min}} = kS_b/S$  ( $k = 3$ ,  $S$  = the line slope and  $S_b = \text{SD}$ ) of 20 replicated determinations of reagent blanks was used to calculate the detection limit of  $\text{Cu}^{\text{II}}$  to be  $0.04 \mu\text{g cm}^{-3}$ .

**Effect of Foreign Ions on  $\text{Cu}^{\text{II}}$  Determination.** – Because of the presence of excess  $\text{Co}^{\text{II}}$ , no masking reagent was added. We have observed that none of the following ions affected direct determination of  $0.400 \mu\text{g cm}^{-3}$   $\text{Cu}^{\text{II}}$  (error  $< 10\%$ ):  $80 \mu\text{g cm}^{-3}$   $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ;  $20 \mu\text{g cm}^{-3}$   $\text{Al}^{3+}$ ,  $\text{V}^{5+}$ ,  $\text{Mo}^{6+}$ ,  $\text{Cr}^{3+}$ ;  $10 \mu\text{g cm}^{-3}$   $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $4 \mu\text{g cm}^{-3}$   $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{3+}$ .

**Analysis of Copper(II) in River and Waste Water.** – To test the method,  $\text{Cu}^{\text{II}}$  was determined in two samples: river water and wastewater. Six replicated determinations of each sample were carried out and two replicated standard additions of each sample were made to check the accuracy of the recommended method. The final results are given in Table II. It is seen that the recovery of  $\text{Cu}^{\text{II}}$  is between  $91.0$  and  $106\%$  and the RSD is less than  $5.58\%$ . Therefore, the recommended method is accurate and selective.

TABLE II. Determination of  $\text{Cu}^{\text{II}}$  in two different water samples with  $\text{Co}(\text{CNBAC})_2$  as the chromogenic reagent

Sample	$\gamma(\text{Cu}^{\text{II}}) / \mu\text{g cm}^{-3}$		RSD %	Recovery %
	Added	Found		
Wastewater	0	$0.105 (\pm 0.006)^{(a)}$	5.58	106–91.0
	0.100	0.211–0.196	–	–
River water	0	$0.618 (\pm 0.009)^{(a)}$	1.53	104–93.2
	1.00	1.66–1.55	–	–

<sup>(a)</sup> Average of six determinations, standard deviation in parentheses.

### CONCLUSIONS

The spectral correction technique is, in fact, one of the dual-wavelength spectrophotometric methods, but different from the others<sup>16–19</sup> in operation. Not only does it give an accurate determination of a trace metal (M), but also the calculation of stability constants of a complex becomes simple. Because the current chromogenic reagent (L) itself often has a very high molar absorption coefficient, its light absorption occupies a large and assignable fraction. Solely the free L maintains a strict dynamic equilibrium of the reaction between M and L. The



spectral correction technique may provide the absorbance fraction of each of the colour mixtures, so that the formation constants of the complex are determined easily. The competition coordination reaction is often applied in analytical complexometry, *e.g.*, complexometric titration. The spectral correction technique makes the competition coordination more suitable for high selectivity spectrophotometry. We believe that the combination of the CCSD and the spectral correction technique will play an important role in a selective spectrophotometric approach.

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## SAŽETAK

### Konstante stabilnosti kompleksa kobalta(II) i bakra(II) s 3-[(*o*-karboksi-*p*-nitrobenzen)azo]kromotropnom kiselinom i selektivno određivanje bakra(II) kompeticijskom koordinacijom

Hong-Wen Gao i Jian-Fu Zhao

Reakcije između bakra(II) i kobalta(II) s 3-[(*o*-karboksi-*p*-nitrobenzen)azo]kromotropnom kiselinom (CNBAC) bile su primjetljive pri pH = 11,4. Rezultati su pokazali nastajanje dvaju kompleksa, Co(CNBAC)<sub>2</sub> i Cu(CNBAC), čije su kumulativne konstante stabilnosti iznosile  $5,22 \times 10^9 \text{ dm}^3 \text{ mol}^{-1}$  odnosno  $7,61 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ , a njihovi molarni apsorpcijski koeficijenti  $1,19 \times 10^4$ , odnosno  $2,12 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  kod 610 nm. Kompeticijska koordinacija bakra(II) i kobalta(II) s CNBAC primijenjena je za selektivno određivanje bakra(II) spektralnom korekcijskom tehnikom. U odsutnosti maskirajućih reagensa, ta je metoda selektivna i iskorištena je za kvantitativno određivanje bakra(II) u uzorcima riječne i otpadnih voda.