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## Investigation of the Property Constants of Both Al and Cu Complexes with Picramine Ca and Using Competition Coordination for the Selective Determination of Trace Amounts of Cu<sup>1</sup>

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**Abstract**—The reactions between Cu(II) and picramine CA (PCA) and Al(III) and PCA were both sensitive at pH 7. The competition coordination between Cu and the Al–PCA complex was applied to the selective determination of Cu (CCSD) by the spectral correction technique. Results have shown that the complexes formed at pH 7 are Al<sub>2</sub>(PCA) and Cu(PCA)<sub>3</sub>, their cumulative stability constants are  $4.43 \times 10^5$  and  $2.08 \times 10^{15}$ , respectively, and their real molar absorptivities are  $5.78 \times 10^3$  at 650 nm and  $3.19 \times 10^4$  at 530 nm. At the analysis of the samples, the relative standard deviation (RSD) was 5.0% and the recovery rate of Cu was between 94 and 108%.

Copper often exists in wastewater, ore, metal material, and so on. The reagents 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [1], dithizone, di-2-pyridylmethanone-2-(5-nitropyridyl)hydrazone [2], and others are used in the determination of copper by spectrophotometry. The ligand picramine CA (PCA) was earlier used in the determination of Zr [3], RE [4], Sc [5], and so on. The structure of PCA is given below:



This reagent can react with many metals, for example, Ti(IV), Co(II), Pb(II), Fe(II), Cu(II), Cd(II), Al(III), V(V), etc. In order to determine a certain metal, several masking reagents are often added simultaneously. This often brings out many troubles in operation and causes a decrease in the sensitivity. In the present work, the competition coordination for selective determination (CCSD) [6-8] was applied. It uses a kind of metal ions  $(M_1)$  to substitute for another metal element  $(M_2)$  from the M<sub>2</sub>-R complex. Because a great amount of M<sub>2</sub> exists in solution, the complexation of other metals with R is difficult, except for M<sub>1</sub>. Cu(II), Ti(IV), and Fe(II, III) have a stronger complexation with PCA than Al(III) at pH 7. So Cu(II) may substitute Al from its PCA complex in the presence of Tiron, which may mask Ti and Fe, and this substitution has been applied to the detection of Cu traces in samples with satisfactory results. The spectral correction technique [9–13] has been applied to the competition coordination reaction instead of ordinary spectrophotometry because it may eliminate the interference of the excessive PCA. The determination of the property constants of both Cu and Al complexes with PCA is easier and simpler than the conventional methods, e.g., the molar ratios [14], continuous variations [15], equilibrium movements [16], etc. Results showed that the composition ratios of Al and Cu to PCA are 2 : 1 and 1 : 3 and their cumulative stability constants are  $4.43 \times 10^5$  and  $2.08 \times 10^{15}$ .

## **EXPERIMENTAL**

Apparatus and reagents. Absorption spectra were recorded with a UV/VIS 265 spectrophotometer (Shimadzu, Kyoto, Japan) and the independent absorbance of the solution was measured with a Model 722 spectrophotometr (Shanghai 3rd Instruments), both with 1.0-cm cells. A DDS-11A conductivity meter (Tianjin 2nd Analytical Instruments) was used to measure conductivity together with a DJS-1 conductivity immersion electrode (electrode constant 0.98) (Shanghai Tienkuang Device Works) in the medium of deionized water of 0.5–1  $\mu\Omega^{-1}$  cm. The pH of the solution was measured with a pHS-2C acidity meter (Leici Instruments, Shanghai, China) and a Model 620D pH Pen (Shanghai Ren's Electronics).

Standard Cu(II) and Al(III) solutions, both 100.0 mg/L, were prepared by dissolving 0.100 g of the high-purity metals (content >99.9%) in 10 mL of 5 mol/L hydrochloric acid and 5 mol/L of nitric acid and then diluting them to 1000 mL with deionized water. Standard Cu(II) and Al(III) solutions, both 10.0 mg/L, were prepared daily. The standard PCA solution, 1.00 mM, was prepared by dissolving 0.2650 g

<sup>&</sup>lt;sup>1</sup> This article was submitted by the author in English.

A

0.25

0.20

0.15

0.10

0.05

0



Fig. 1. Absorption spectra of PCA and its Al and Cu complexes in 25 mL of solution at pH 7: (1) PCA (0.500 µmol), (2) Al (20.0 µg)-PCA (1.00 µmol) solution, (3) Cu (10.0 µg)-PCA (1.00 µmol) solution, (4) Al (200 µg)-PCA (0.50 µmol) complex (no free PCA), (5) Cu (500 µg)-PCA  $(0.50 \ \mu mol)$  complex (no free PCA) and (6) Cu (10.0 \ \mu g) solution initially containing the Al-PCA complex (1.30 µmol). 1, 4, and 5 against water and the others against blank references.

of purified picramine CA (PCA, Shanghai Changke Reagents Institute) in 500 mL of deionized water. It was stored in a dark bottle at 5°C. The Al-PCA complex solution, 0.500 mM, was prepared by mixing 100 mL of 1.00 mM PCA solution and 100 mL of 2.0% aluminum potassium sulfate. After 30 min, it can be used as a novel chrmogenic reagent in CCSD of Cu. The buffer solution, pH 7, was prepared with ammonium acetate to adjust the acidity of the solution. The masking reagent, 0.5% Tiron was prepared by dissolving 0.5 g of 1,2-dihydroxybenzene-3, 5-disulphonic acid disodium (Shanghai 3rd Reagents) in 100 mL of deionized water; it was used to mask Ti(IV) and Fe(II, III).

Recommended methods. For the determination of the property constants of the complexes: To a 25-mL volumetric flask, add 2.5 mL of pH 7 buffer solution and a known volume of PCA solution. Add 10.0 µg of Cu(II) or 40.0 µg of Al(III). Dilute to volume and mix well. After 30 min, measure the absorbances at 595 and 650 nm (Al-PCA reaction) or 530 nm (Cu-PCA reaction) against a reagent blank, respectively, and then calculate  $A_c$  of the complexes by the following relation:

$$A_{\rm c} = (\Delta A - \beta \Delta A')/(1 - \alpha \beta),$$

where  $\alpha = \varepsilon_{MB_{\nu}}^{\lambda_1}$  and  $\beta = \varepsilon_R^{\lambda_2} / \varepsilon_R^{\lambda_1}$ . Here, the symbols  $\Delta A$ and  $\Delta A'$  are the absorbances of the solution at 650 or 530 nm and 595 nm against a reagent blank, respectively. Both  $\alpha$  and  $\beta$  are correction constants. The symbols  $\varepsilon_{MR_{\gamma}}^{\lambda_1}$ ,  $\varepsilon_{MR_{\gamma}}^{\lambda_2}$ ,  $\varepsilon_R^{\lambda_1}$ , and  $\varepsilon_R^{\lambda_2}$  are the molar absorptivi-



(a)

bance of the reacted solution (a), the effective fraction  $(\eta, \%)$ of PCA (b), and the complex ratio ( $\gamma'$ ) of the complexes (c) at pH 7: (a)  $\hat{I}$ , Al (40.0 µg)–PCA solution measured at 650 nm; 2,  $A_c$  of the Al (40.0 µg)–PCA complex at 650 nm; 3, Cu  $(10.0 \,\mu\text{g})$ –PCA solution measured at 530 nm; and 4,  $A_c$  of the Cu (10.0  $\mu$ g)–PCA complex at 530 nm. (b) 1, Al (40.0  $\mu$ g) and 2, Cu (10.0 µg). (c) 1, Al (40.0 µg) and 2, Cu (10.0 µg).

ties of both the Al-PCA and Cu-PCA complexes and PCA at 595 and 650 or 530 nm, respectively.

Determination of Cu: To a 25-mL volumetric flask, add a known volume of a sample containing less than 20.0 µg of Cu(II). Add 2.5 mL of pH 7 buffer solution, 1 mL of the masking reagent solution and 3.00 mL of 0.500 mM Al-PCA complex. Dilute to volume and mix well. After 30 min, measure the absorbances at 650 and 530 nm against a reagent blank and then calculate  $A_{\rm c}$  of the Cu-PCA complex.

## **RESULTS AND DISCUSSION**

Spectral analysis. Figure 1 shows the absorption spectra of PCA and its Cu and Al complex solutions at

3.0



**Fig. 3.** Effect of the pH on the Ac of both the Al–PCA and Cu–PCA complexes: (1)  $A_c$  of the Al–PCA complex at 650 nm and (2)  $A_c$  of the Cu–PCA complex at 530 nm.

pH 7. From curve 1, the peak absorption of PCA is located at 595 nm. From curves 4 and 5, the peak absorption of the Al-PCA and Cu-PCA complexes is located at 650 and 530 nm, respectively. The peak of spectrum 2 is located at 650 nm, and its valley, at 595 nm. The two wavelengths 650 and 595 nm were used in the determination of the property constants of the Cu-PCA complex. In a similar manner, the peak of spectrum 3 is located at 530 nm, and its valley, at 595 nm. The two wavelengths 530 and 595 nm were selected in the determination of the property constants of the Al-PCA complex. In fact, the spectral correction technique is one of the dual-wavelength spectrophotometric methods, but it is different from the others [17–20] in principle and operation. The correction coefficients were calculated to be  $\beta_{1-PCA} = 0.068$  (A650/A595 nm) and  $\beta_{2\text{-PCA}}$  = 0.820 (A530/A595 nm) from curve 1,  $\alpha_{AI-PCA} = 1.65$  (A595/A650 nm) from curve 4, and  $\alpha_{Cu-PCA} = 0.481 (A595/A530 \text{ nm})$  from curve 5. Therefore, the following relations were used for the  $A_c$  calculation of both the Al-PCA and Cu-PCA complexes:  $A_{c}(Al-PCA) = 1.14(\Delta A - 0.068\Delta A')$  at 650 nm and  $A_{c}(Cu-PCA) = 1.65(\Delta A - 0.820\Delta A')$  at 530 nm.

Effect of the PCA concentration. The effect of the addition of 1.00 mM PCA is shown in Fig. 2a. From curves 1 and 3, it is difficult to use the molar ratios method [14] to determine the accurate complex ratio of PCA to Cu and Al because of the unclearness of the inflexion point. By comparing curve 2 with 1 and 4 with 3, the  $A_c$  of both the complexes is always more than the  $\Delta A$  of the solutions. The difference between  $A_c$  and  $\Delta A$  is often ignored in ordinary spectrophotometry. However, is very valuable to the determination of the property constants of a complex by the spectral correction technique. The effective fraction ( $\eta$ , %) of PCA and the



Fig. 4. The effect of the Al concentration on the ratio of the absorbance of the Al–PCA ( $1.50 \mu$ mol) solution measured at 595 nm to that at 650 nm against water.

molar ratio ( $\gamma$ ') of the effective PCA to Cu or Al are calculated by means of

 $\eta = (A_c - \Delta A)/A_0$  and  $\gamma' = \eta (c_R/c_M)$ .

Here, the symbols  $c_{\rm M}$  and  $c_{\rm R}$  indicate the initial molarity of Cu or Al and PCA and  $A_0$  is the absorbance of the PCA solution against water. Their curves are shown in



**Fig. 5.** Effect of addition of 0.500 mM Al–PCA complex on: (a)  $A_c$  of the Cu–PCA complex at 530 nm and (b) the effective fraction ( $\eta$ , %) of 0.500 mM Al–PCA complex in the presence of 10.0 µg of Cu.

Fig. 2b and 2c. From Fig. 2c,  $\gamma'$  of PCA to Al approaches a maximum at 0.5 when the addition of 1.00 mM PCA is more than 2.0 mL and  $\gamma'$  of PCA to Cu approaches a constant at 3 when the addition of 1.00 mM PCA is more than 0.45 mL. Therefore, complexes of both Al<sub>2</sub>(PCA) and Cu(PCA)<sub>3</sub> were formed here. From Fig. 2b,  $\eta$  of PCA is about 35% in the solution containing 40 µg of Al and 2.00 mL of 1.00 mM PCA and only 24% in the solution containing 10 µg of Cu and the same PCA as above. So the excess PCA occupies 65% in the PCA–Al solution and 76% in the PCA–Cu solution. It is inevitable for such excessive PCA to seriously interfere with the accurate measurement of the complexes. So, the spectral correction technique was applied in this study.

Effect of the pH and time. The effect of the pH of the solution is shown in Fig. 3. The  $A_c$  of the Cu–PCA solution remains constant and maximum between pH 4 and 9.2 from curve 2 and that of the Al–PCA solution shows a peak between pH 6 and 7 from curve 1. So the pH 7 buffer solution was selected in this study. The observation shows that the reaction between Cu and PCA is complete in 20 min and remains constant for at least 2 h and the reaction between Al and PCA is over 30 min. In this study, the measurement of the solution was carried out after 30 min.

**Determination of the stability constant and absorptivity:** The *n*-step stability constant  $(K_n)$ , the general stability constant *K*, and the *n*-step absorptivity of the complexes are calculated by the equations

$$K_n = [\gamma + 1 - n]/(n - \gamma')(c_R - \gamma' c_M);$$
  

$$K = \prod_{n=1}^{\gamma} K_n; \text{ and}$$
  

$$\epsilon_{MR_n}^{\lambda_2} = A_c / [\delta c_M(\gamma' + 1 - n)] - (n - \gamma') \epsilon_{MR_{n-1}}^{\lambda_2} / \gamma' + 1 - n.$$

Here, the symbol *n* indicates the step number of the complex and  $\delta$  is the thickness (cm) of the cell used. The following solutions were prepared for the determination of the property constants of both Al-PCA and Cu–PCA complexes: 40.0 µg of Al plus 1.50 µmol of PCA, and 2.00 µg of Cu plus 0.030, 0.050, and 0.070 µmol of PCA. All measurements were made at 20°C at 0.1 M ionic strength. Three replicated determinations of each were made, and the results are given in Table 1 (n = 3). The cumulative stability constants of both Al<sub>2</sub>(PCA) and Cu(PCA)<sub>3</sub> complexes were calculated to be  $4.43 \times 10^5$  and  $2.08 \times 10^{15}$ . From the stability constants, we know that Cu(PCA)<sub>3</sub> is much more stable than complex  $Al_2(PCA)$ . It is possible for Cu(II) to substitute Al from its PCA complex. From the absorptivity in Table 1, the reaction between Cu and PCA is very sensitive.

Effect of the operation conditions. From curve 6 in Fig. 1, the two wavelengths 650 and 530 nm were selected as the work wavelengths in the CCSD of cop-



Fig. 6. Effect of the substitution time on  $A_c$  of the Cu–PCA complex at 530 nm.



**Fig. 7.** Calibration graphs for the CCSD of Cu at pH 7: (1)  $\Delta A$ , directly measured at 530 nm and (2)  $A_c$  of the Cu–PCA complex at 530 nm.

per. The possible substitution reaction is expressed as follows:

Al–PCA reaction:  $2Al^{3+} + R^{2-} = Al_2R^{4+}$ ;

Cu substitution:  $Cu^{2+} + 3Al_2R^{4+} = CuR_3^{4-} + 6Al^{3+}$ .

The correction constant is calculated to be  $\beta_{Al-R} = 0.965 (A530/A650 \text{ nm})$  from curve 4 in Fig. 1 and  $\alpha_{Cu-R} = 0.124 (A650/A530 \text{ nm})$  from curve 5. The  $A_c$  of the Cu–PCA complex at 530 nm was calculated by the relation  $A_c = 1.14(\Delta A - 0.965\Delta A')$ .

The effect of the Al concentration on the formation of the Al–PCA complex is shown in Fig. 4. The ratio of absorbance of the solution measured at 595 nm to that at 650 nm approaches a mineral constant when the Al molarity is over 5 times that of the PCA, where the free PCA approaches zero. So the Al–PCA complex solution containing 0.500 mM PCA prepared in the Experimental Section was used in SCCD of Cu. The effect of 0.500 mM Al–PCA complex on  $A_c$  of the Cu–PCA complex is shown in Fig. 5a. The  $A_c$  approaches the maximum constant when the addition of 0.500 mM Al–PCA complex is more than 2.0 mL. So 3.0 mL of

<i>n</i> -th	Al <sub>2</sub> (PCA)		Cu(PCA) <sub>3</sub>	
	K <sub>n</sub>	ε at 650 nm	K <sub>n</sub>	ε at 530 nm
1	$4.43 \times 10^{5}$	$5.78 \times 10^3$	$6.90 \times 10^{5}$	$1.08 \times 10^{4}$
2			$1.13 \times 10^5$	$2.01 \times 10^4$
3			$0.27 \times 10^5$	$3.19 \times 10^{4}$

**Table 1.** Determination of the property constants of both Cu–PCA and Al–PCA complexes at pH 7 and 20°C

Table 2. Determination of Cu in samples

Sample	Added, mg/L	Found, mg/L	RSD, %
Synthetic	0	$0.237 \pm 0.007$	2.8 (100–108)
sample	0.200	$0.444 \pm 0.006$	
Wastewater	0	$0.100\pm0.005$	5.0 (94.0–104)
	0.100	$0.198\pm0.006$	

0.500 mM Al–PCA complex was added in the quantitative determination of trace amounts of Cu. The fraction ( $\eta$ , %) of the effective Al–PCA complex is shown in Fig. 5b. Approx. 64% of the Al–PCA complex was substituted by Cu and 36% of the Al–PCA complex is surplus in the solution. Of course, the excess of the Al–PCA complex will affect the accuratcy of the measurement of the substitution solution. So ordinary spectrophotometry is unsuitable in the measurement of the substitution solution, too.

**The effect of the substitution time** on the Ac of the Cu–PCA complex is shown in Fig. 6. The Ac decreases slowly but approaches a constant after 30 min. So, the solution was measured after 30 min.

**Calibration graph.** A series of standard Cu  $(0-30.0 \ \mu g)$  solutions were prepared and the absorbance of each was measured and plotted as shown in Fig. 7. All of the  $A_c$  points are much more linear than the measurement points in the range between 0 and 20.0  $\mu g$  of Cu. The slope of line 2 is more than twice that of line 1. So the spectral correction technique has the higher sensitivity and better accuracy than ordinary spectrophotometry.

**Precision and the detection limit of copper.** Six replicate determinations of the standard solutions containing 2.00 and 20.00 µg of Cu were carried out. The results are as follows:  $1.98 \pm 0.06$  and  $19.4 \pm 0.4$  µg of Cu (n = 6). However, the ordinary spectrophotometry gives  $1.44 \pm 0.30$  and  $15.8 \pm 2.0$  µg of Cu. For  $A_c = 0.010$ , the detection limit of the method was calculated to be only 0.5 µg of Cu.

Effect of the foreign ions. Because the novel chromogenic reagent solution contains a great amount of existing Al(III) and a lack of free PCA, it is possible that most of the metal ions no longer react with PCA. We found that only Cu(II), Ti(IV), and Fe(II, III) can substitute for Al from the Al–PCA complex. Both Ti and Fe can be masked by Tiron. Once the recommended method was carried out, none of the following metal ions affect the direct determination of 10  $\mu$ g of Cu(II) (<10% error): 1 mg of Ba, Ca, and Mg; 0.1 mg of Cd, Mn, Zn, Co, Pb(II), Ni, Hg(II), Cr(III), and Mo(VI); and 0.05 mg of Fe(II, III), Ti(IV), and V(V). So the method is selective in the detection of trace amounts of Cu.

**Sample analyzed.** As a test of the method, Cu was determined in samples and the results are given in Table 2. The recovery of Cu is between 94.0 and 108% and the RSD is less than 5.0%.

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