Substitution Coordination Approach for Selective Determination of Complex: Pontachrome Violet SW/Fe(III)/Cu(II) System

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The Substitution Coordination for Selective Determination (SCSD) was proposed by studying the complexations of pontachrome violet SW (PCV) with Fe(III) and Cu(II) at pH 5.5. The updated approach to the determination of binding constants of a complex was established by the spectral correction technique (SCT). The substitution complexation Cu(II) + Fe(PCV) → Cu(PCV) + Fe(III) has been applied to the direct selective determination of copper traces by the SCT with a high sensitivity.

INTRODUCTION

The spectral correction technique (SCT) has been applied extensively in study of analytical, complex, and supramolecular chemistry.\textsuperscript{1,2} However, it can increase the accuracy and precision but not improve the selectivity in trace analysis. For this purpose, the substitution coordination approach was proposed, and it indicates a metal to substitute for another metal from its complex. The former metal ions must have a much stronger complexation with the selected ligand than most other metal ions. This method may give a high selectivity in trace analysis. Here, the reaction of copper(II) to substitute Fe(III) from its pontachrome violet SW (PCV) complex at pH 5.5 has been investigated in detail and used in the quantitative determination of Cu in samples with satisfactory results by the SCT. Additionally, an approach to the determination of binding constants of a complex was given, too.

PRINCIPLE AND CALCULATION

At the coordination equilibrium: \( N \text{L (Ligand)} + M \text{ (Metal)} \leftrightarrow ML_N \) (complex), the molar ratio \((\gamma)\) of the effective L to M, the molar concentration \((C_L)\) of free L are calculated by reactions (1) and (2). The complexation of L with M may be regarded as a particular Langmuir monolayer adsorption\textsuperscript{3} of L on M but the binding force is chemical bond not electrostatic at tration. So the index for the reaction ratio of L to M and the binding constant \((K, \text{ different from equilibrium constant})\) of complex \(ML_N\) are obtained by re gressing \(\gamma^2\) vs. \(C_L^{-1}\) by relation (3):

\[ \gamma = \frac{\alpha \Delta A - \Delta A'}{\delta \epsilon L (1 - \alpha \beta) C_M} \]  
\[ C_L = C_L0 - \frac{\alpha \Delta A - \Delta A'}{\delta \epsilon L (1 - \alpha \beta)} \]  
\[ \frac{1}{\gamma} = \frac{1}{N} + \frac{1}{KNC_L} \]

Here the symbols \(\Delta A\) and \(\Delta A'\) are the absorbances of the solution, respectively measured at peak and valley wave lengths \(\lambda_2\) and \(\lambda_1\). The correction constants \(\alpha\) and \(\beta\) may be calculated.

EXPERIMENTAL SECTION

Apparatus and Reagents

Absorption spectra were recorded on a TU1901 Spectro photometer (PGeneral, Beijing) and in dependence absorbance was measured on a Model 722 spectrophotometer. A DDS-11A conductivity meter, (Tianjin Second Analytical Instruments) was used to measure conductivity to gether with DJS-1 conductivity immersion electrode (electrode constant 0.98) (Shanghai Tienkuang Instruments) in product of deionized water of less than 0.5 \(\mu\)Sm. The pH of the solution was measured with a Delta 320-S pH meter (Mettler Toledo).

Stock standard solutions of Cu (100.0 mg/L) and Fe (100.0 mg/L) were prepared by dissolving their high purity metals in concentrated nitric acid and diluting with deionized water.
water. The PCV solution (0.700 mmol/L) was prepared by dissolving 0.2478 g of pontachrome violet SW (PCV) in 50 mL of DMF and then diluting to 500 mL with deionized water. Standard Cu(II) and Fe(III) solutions (10.00 µg/mL) were prepared by diluting the above solutions. The acetic buffer solution (pH 5.5) was used to adjust the acidity of the solution. The Fe(PCV) solution (0.200 mmol/L) by mixing 14.3 mL of 0.700 mmol/L PCV, 28.6 mL of the stock standard Fe(III) solution and 5 mL of pH 5.5 buffer solution and diluting to 50.0 mL. In this solution, only Fe(PCV) but not Fe(PCV)$_2$ is formed because it contains highly excessive and free Fe(III).

**General Procedures**

*Determination of property constants of Fe and Cu with PCV:* Into a 10 mL calibrated flask were added 10.00 µg of Fe(III) or Cu(II), 1.0 mL of the buffer solution and an appropriate volume of 0.700 mmol/L PCV. The mixture was diluted with deionized water to 10 mL and mixed thoroughly. After 5 min, absorbances of the solutions were measured at 520 and 445 nm, respectively, against the reagent blank and treated in the same way without Fe(III) or Cu(II), and then $A_c$ of the complex was calculated.

*Quantitative Determination of Cu:* A known volume of a sample solution containing less than 20 µg of Cu was added into a 10-mL volumetric tube along with 1.0 mL of the pH buffer solution and a certain volume of Fe(PCV) solution. After 10 min, measured absorbances at 520 and 445 nm with 2-cm cell, respectively, against the reagent blank treated in the same way without Cu and then $A_c$ of the substitution complex was calculated.

**RESULTS AND DISCUSSION**

**Spectral analysis**

The reactions between PCV and Fe(III) and Cu(II) at pH 5.5 were carried out and the absorption spectra are shown in Fig. 1. From curves 1, 2 and 3, the spectral peak of PCV, Fe-PCV and Cu-PCV complexes are located at 490, 520 and 460 nm, respectively. From curves 4 and 5, the two wavelengths: both 520 and 445 nm should be selected in this work. From curves 1, 2 and 3, the correction constant was calculated to be $\beta_{PCV} = 0.521$ and $\alpha_{PCV} = 0.471$. $\beta_{PCV} = 1.94$ and $\alpha_{PCV} = 0.254$. So the real absorbance ($A_c$) of complex ML is calculated$^3$ by $A_c = 1.33(A - 0.521A')$ in the Fe-PCV solution and $A_c = 1.95(A - 1.94A')$ in the Cu-PCV solution.

**Determination of Fe-PCV and Cu-PCV Complexes**

By varying the addition of PCV in Fe (10.0 µg) and Cu (10.0 µg) solutions, $\gamma$ vs. $C_L$ and $\gamma^{-1}$ vs. $C_L^{-1}$ are shown in Fig. 2.

![Graph 1](image1.png)

*Fig. 1.* The absorption spectra of PCV, PCV-Cu(II), PCV-Fe(III) and PCV-Fe-Cu solutions at pH 5.5: 1- PCV; 2- Fe-PCV and 3- Cu-PCV complexes; 4- Fe-PCV and 5- Cu-PCV solutions against the PCV solution; 6- Fe(PCV)-Cu solution against the Fe(PCV) solution.

![Graph 2](image2.png)

*Fig. 2.* $\gamma$ variation in Fe-PCV (1) and Cu-PCV (2) solutions and $\gamma^{-1}$ vs. $C_L^{-1}$ [3- Fe(PCV)$_2$ and 4- Cu(PCV)].
2. From curves 1 and 2, we also observe that both γ approach the maxima at N = 2 and 1, respectively. So the final complexes: Fe(PCV)₂ and Cu(PCV) are formed. From the slope rate of lines 3 and 4, the anastomotic results were observed. The binding constant of Fe(PCV)₂ was calculated to be $K = 1.95 \times 10^4$ and that of Cu(PCV) is $K = 5.46 \times 10^5$. In addition, from the slope of lines 3 and 4, we confirm the same binding ratio of the complexes as those above. Therefore, we believe that the recommended calculation of the binding constants of a complex is simpler and more reliable than the conventional methods.⁵,⁶

**Substitution of Fe by Cu**

From the two $K$ values above, Cu(II) may substitute Fe(III) from its PCV complex because $K$ of the Cu-PCV complex is near to 30 times that of the Fe-PCV complex. This substitution phenomenon has been observed in the experiment. The substitution reaction is suggested as followed:

$$\text{Cu(II)} + \text{Fe(PCV)} \rightarrow \text{Cu(PCV)} + \text{Fe(III)}.$$  

A large excess of Fe(III) was added into the PCV solution to make the coordination complete, forming Fe(PCV). Such a solution contains only both Fe(III) and Fe(PCV). The expected metal ratio has indicated no free PCV in the solution containing Fe(III) more than 5 times molarity of PCV. In such a solution, the addition of other metals has been found not to alter its absorption spectrum except for Cu(II). Therefore, the substitution complexation may be used for the selective determination of Cu traces.

**Quantitative Determination of Cu**

The solution mixed 1.00 mmol/L Fe(III) with 0.200 mmol/L PCV forms 0.200 mmol/L Fe(PCV) complex at equilibrium. It was used as a new stain for the determination of Cu traces. Many metal ions, such as Pb(II), Zn(II), Ni(II), Cd(II), Al(III), Hg(II), rare earth, alkali earth metals and normal anions, have not been found to interfere with the direct determination of Cu. The calibration graphs are shown in Fig. 3. We observe that lines 1 and 2 have much poorer linearity and less slope rate than line 3. Therefore, the SCT is more suitable to a substitution complexation than ordinary spectrophotometry. The approach has been applied to analysis of wastewater samples and it gave identical results with the AAS.

**TREND AND FOREGROUND**

The SCT and SCSD provide a very helpful experimental strategy for the determination of binding constants of a metal complex and trace analysis even though the sensitivity is lower than the other methods, e.g. RLS.⁷ We believe that the cooperation of the SCT and other methods, e.g. flow injection analysis (FIA) and fluorimetry, will improve sensitivity and understanding that the class of calcium spectrophotometry may still play an important role in study of the coordination of a ligand with metal or a probe with macromolecule.

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**Key Words**

Substitution Coordination for Selective Determination; Spectral correction technique; Binding constants; Detection of Cu traces.

**REFERENCES**