Articles

Spectrophotometric Investigation of Cu and Fe Complexes with *o*-Chlorophenylfluorone and Selective Competition Coordination Determination of Iron Traces

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The two reactions between iron ion (Fe^{3+}) and *o*-chlorophenylfluorone (*o*-CPF) and copper ion (Cu^{2+}) and *o*-CPF are sensitive at pH 6 in the presence of Triton X-100. We have determined the formation constants of the complexes by the spectral correction technique. Because of the poor selectivity of o-CPF to metals, the competition coordination of only the iron ion from the Cu-o-CPF complex was found and applied to the selective detection of iron traces by the Selective Competition Coordination Determination (SCCD) approach. The analysis of several samples shows that the relative standard deviations are less than 5.0% and the recovery of iron ions between 94.5% and 106%.

Keywords : Selective competition coordination determination, Spectral correction technique, Iron, Copper, *o*-Chlorophenylfluorone.

Introduction

Iron (Fe) ions exist extensively in nature. They can react sensitively with a lot of ligands or chromogenic agents such as 2-(5-brom*o*-2-pyridylazo)-5-diethylaminophenol[1], *o*-phenanthroline,[2] 2,3-dihydroxynaphtalene[3] and so on.[4-12] The synthesis of a phenylfluorone derivant, *o*-chlorophenylfluorone (*o*-CPF) was reported[13] with the following structure:
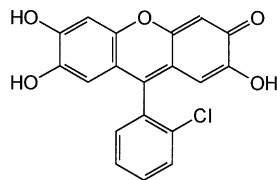
It may complex many metals between pH 3 and 7, for example, titanium, vanadium, aluminum, manganese, tin, copper, iron etc. Therefore, its selectivity is deemed poor. The determination of a metal was possible only when many masking reagents were added simultaneously. The Selective Competition Coordination Determination (SCCD) is a novel approach earlier reported.[14,15] This technique uses a metal to substitute another metal ion from its complex so as to improve the selectivity of the detection of metal traces. We found that iron has a stronger complexation with *o*-CPF than other metals. It can substitute other metals from their (their or its???) *o*-CPF complex. In the present work, copper (II) was selected. The process is described as follows: at first enough copper (II) was added to completely complex *o*-CPF then iron (II, III) was added to substitute the complexed Cu to form the Fe-*o*-CPF complex. The spectral correction technique[16-18] must be applied because of interference from the excessively high Cu-*o*-CPF complex instead of ordinary spectrophotometry. The determination of the property constants of the Fe and Cu complexes with *o*-CPF were also carried out and such a technique appears more understandable in principle and simpler in operation than the classical methods, such as the molar ratios,[19] continuous variations,[20] etc. Results show that the composition ratio of Cu and Fe to *o*-CPF was Cu : *o*-CPF = 1 : 1 and Fe : *o*-CPF = 1 : 4, respectively, at pH 6 in the presence of Triton X-100. Their cumulative stability constants are 7.86×10^4 and 3.36×10^{24}, respectively. The real absorbance of the Fe-*o*-CPF complex is linear in the range 0-10.0 mg/L Fe. This approach was applied to analyze iron in food and water, with satisfactory results.

Experimental Section

Apparatus and Reagents. Absorption spectra were recorded with a TU1901 spectrophotometer (PGeneral, Beijing) using 10- mm glass cells, and single absorbance was measured with a Model 722 spectrophotometer (Shanghai).

Standard Fe ion (III) stock solution, (100 mg/L) was prepared by dissolving 0.100 g of the high-purity metal in nitric acid and dilution to 1000 mL. Standard Fe(III) use solution (2.00 mg/L) was prepared daily by diluting the above solution.

Copper sulfate solution, 0.05% was prepared to complex *o*-CPF and to form the new ligand.

The ligand solution, 1.00 mmol/L *o*-CPF was prepared by dissolving 0.319 g of *o*-chlorophenylfluorone (*o*-CPF, Changke

Reagents Institute of Shanghai) in 1000 mL of absolute alcohol (A. R., Shanghai Reagents). It was stored in a dark bottle and at less than 5 °C.

The acetate and acetic acid buffer, pH 6.0 solution, was prepared and used to adjust the acidity of the solutions.

The non-ionic surfactant solution, 1% Triton X-100, was used to improve the solubility of the complexes and the sensitivity of the complexations.

Procedures. Determination of the properties of Fe and Cu complexes: To a 25-mL volumetric flask were added 2.5 mL of pH 6 buffer solution, 1 mL of Triton X-100 solution and a known volume of *o*-CPF solution. Also added were 10.0 mg of Fe(III) or 10.0 mg of Cu(II). The solution was diluted to volume and mixed well. After 30 min, absorbances were measured at 560 and 500 nm against a reagent blank. The real absorbance (A_c) was calculated by the relation[15]:

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha \beta} \text{ where } \alpha = \frac{\varepsilon_{ML_\gamma}^{\lambda 1}}{\varepsilon_{ML_\gamma}^{\lambda 2}} \text{ and } \beta = \frac{\varepsilon_L^{\lambda 2}}{\varepsilon_L^{\lambda 1}}$$

The symbols ΔA and $\Delta A'$ are the absorbances of the reaction solution, measured at peak and valley wavelengths, respectively, against the reagent blank. The coefficients α and β are the correction constants. The symbols $\varepsilon_{ML_\gamma}^{\lambda 1}$, $\varepsilon_{ML_\gamma}^{\lambda 2}$, $\varepsilon_L^{\lambda 1}$ and $\varepsilon_L^{\lambda 2}$ are the molar absorptivity of the product and ligand at these two wavelengths, respectively.

Determination of trace amounts of iron: To a 25-mL volumetric flask we added 2.5 mL of pH 6 buffer solution, 1 mL of Triton X-100 solution, 2 mL of 0.05% copper sulfate and 1.0 mL of *o*-CPF solution. After 10 min, the free and unreacted *o*-CPF approaches to zero because Cu has a much higher *o*-CPF molarity. The next step was adding a known volume of a sample containing fewer than 10.0 μg of Fe and dilution to volume. The solution was mixed well for 30 min, and absorbances were measured at 560 and 630 nm against a reagent blank. The real absorbance (A_c) was calculated according to the above expression.

Results and Discussion

Spectral Analysis. Figure 1 gives the absorption spectra of *o*-CPF and its Fe and Cu complex solutions at pH 6.0. The presence of Triton X-100 was found to improve the solubility of complex. At pH 6, *o*-CPF appears orange from curve 1, Fe-*o*-CPF blue from curve 4 and Cu-*o*-CPF red from curve 5. From curve 2 and 3, we select the peak wavelength 560 and the valley wavelength 500 nm as work wavelengths for the determination of property constants of Fe and Cu complexes with o-CPF. The correction coefficient $\beta_{o\text{-CPF}}$ was calculated to be 0.097 from curve 1, $\alpha_{Cu\text{-}o\text{-CPF}}$ 0.456 from curve 5 and $\alpha_{Fe\text{-}o\text{-CPF}}$ 0.941 from curve 4. In SCCD of iron traces, the peak wavelength 560 and the valley wavelength 630 nm should be used from curve 6. One possible substitution process is suggested as follows:
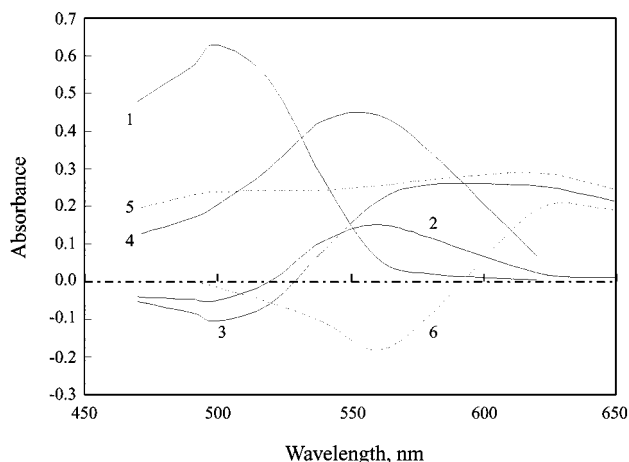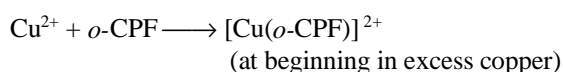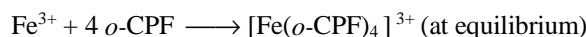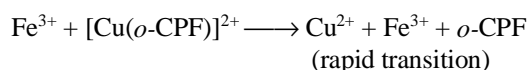
$$Cu^{2+} + o\text{-CPF} \longrightarrow [Cu(o\text{-CPF})]^{2+}$$
(at beginning in excess copper)

Figure 1. Absorption spectra of solutions containing: 1- 1.00 μmol/L *o*-CPF, 2- 10.0 mg of Cu(II) and 1.00 mmol/L *o*-CPF, 3- 10.0 mg of Fe(III) and 1.00 mmol/L *o*-CPF, 4- 200 mg of Cu(II) and 0.50 mmol/L *o*-CPF, 5- 200 mg of Fe(III) and 0.50 mmol/L *o*-CPF, 6- 10.0 mg of Fe(II), 300 mg of Cu(II) and 1.00 mmol/L *o*-CPF. 1-, 4- and 5- against water and the others against reagent blank. Note: 4 - only Cu-*o*-CPF complex and 5-only Fe-o-CPFcomplex at equilibrium.

$$Fe^{3+} + [Cu(o\text{-CPF})]^{2+} \longrightarrow Cu^{2+} + Fe^{3+} + o\text{-CPF}$$
(rapid transition)

$$Fe^{3+} + 4\,o\text{-CPF} \longrightarrow [Fe(o\text{-CPF})_4]^{3+} \text{ (at equilibrium)}$$

This intermediate transition was indicated by the solutions changed to orange (*o*-CPF color) from red (Cu-*o*-CPF color) and then rapidly to blue (Fe-*o*-CPF) when Fe(III) was added. The correction coefficient $\beta_{Cu\text{-}o\text{-CPF}}$ was calculated to be 0.165 (630 nm/560 nm) from curve 5 and $\alpha_{Fe\text{-}o\text{-CPF}}$ was calculated to be 0.962 (560 nm/630 nm) from curve 4. The real absorbance (A_c) of the Fe-*o*-CPF complex at 630 nm can be formulated as: $A_c = 1.17(\Delta A - 0.165\Delta A')$.

Effect of *o*-CPF on Fe and Cu complexes. Figure 2 shows the effect of *o*-CPF solution on the absorption of its
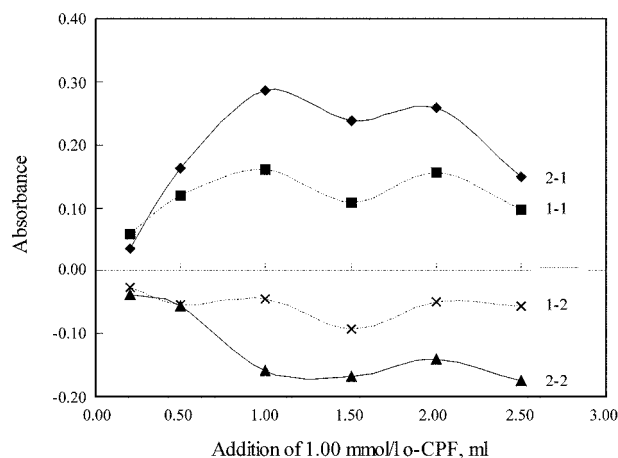

Figure 2. Effect of the addition of 1.00 mmol/L *o*-CPF on the absorbance of solutions: 1-x containing 10.0 μg of Cu(II), 2-x containing 10.0 μg of Fe(III). x-1 measured at 560 nm and x-2 at 500 nm. All against reagent blank.
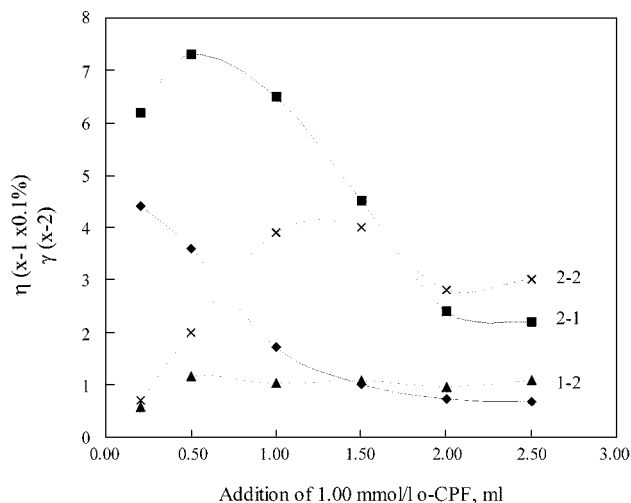
Figure 3. Effect of the addition of 1.00 mmol/L *o*-CPF on η and γ' of solutions containing: 1-x 10.0 μg of Cu(II), 2-x 10.0 μg of Fe(III). x-1- $\eta(\%)$ and x-2- γ'.

Fe and Cu complexes. Curves 1-x reflect the difficulty calculating the complex ratio of Fe and Cu to *o*-CPF accurately by the molar ratios method because of the unclearness of the inflexion point. The effective fraction (η) of *o*-CPF and the complex ratio (γ') of each solution can be calculated by the relations[16]:

$$\eta = \frac{A_c - \Delta A}{A_o} \quad \text{and} \quad \gamma' = \eta \times \frac{C_L}{C_M}$$

The symbols C_M and C_L indicate the molarity of the metal (M) and the ligand (L) in the beginning, and A_o is the absorbance of the blank reagent. Their curves are shown in Figure 3. From curves x-1, γ' of *o*-CPF to Cu approaches to constant at 1 when the addition of *o*-CPF solution is more than 0.5 mL, and that of *o*-CPF to Fe approaches to constant at 4 when the addition of *o*-CPF solution is more than 1.0 mL. Therefore, the two complexes, Cu(*o*-CPF) and Fe(*o*-CPF)$_4$, are formed here. From curves x-2, η of *o*-CPF is about 20% in Cu (10 μg) solution and only 75% in Fe (10
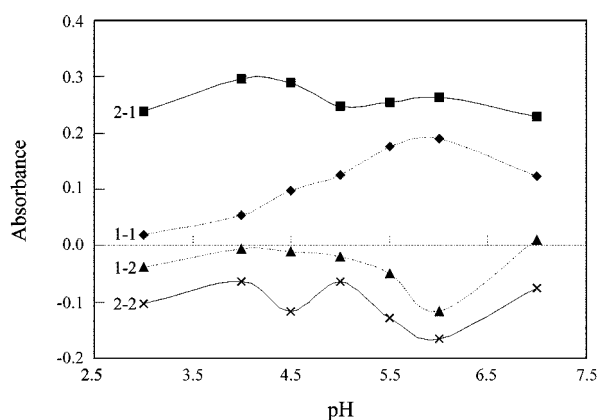

Figure 4. Effect of pH on the absorbance of solutions containing: 1-x 10.0 μg of Cu(II), 2-x 10.0 μg of Fe(III). x-1 measured at 560 nm and x-2 at 500 nm. All against reagent blank.
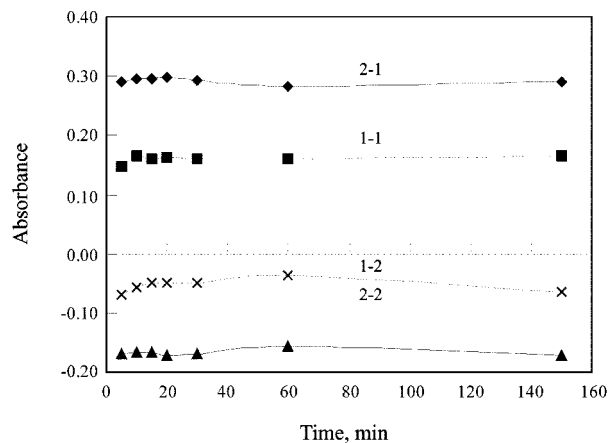

Figure 5. Effect of the reaction time on the absorbance of solutions containing: 1-x 10.0 μg of Cu(II), 2-x 10.0 μg of Fe(III). x-1 measured at 560 nm and x-2 at 500 nm. All against reagent blank.

μg) solution with the addition of 1.0 mL of the o-CPF solution. The excess *o*-CPF reaches 80% and 25%, respectively. Inevitably, such a high amount of free *o*-CPF affects the accurate measurement of absorbance of the complexes. Therefore, ordinary spectrophotometry is not suitable in the present work.

Effect of pH and Time. Effect on the curves by varying the pH of solution, are shown in Figure 4. The absorbance reached maximum and remained constant when the pH was between 5 and 7. In the present study, a pH 6.0 buffer was used. The effect of the reaction time is shown in Figure 5. The curves show the reaction was complete in 20 min. The solution's absorption was found to remain constant for at least 2.5 hours.

Determination of Stability Constant and Absorptivity. The stepwise stability constant (K_n), cumulative (K) and stepwise absorptivity (ε) of the complex can be calculated from the following equations[17]:

$$K_n = \frac{\gamma' + 1 - n}{(n - \gamma')(C_L - \gamma' C_M)} \quad \text{and the cumulative constant (K)}$$

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

$$\varepsilon_{ML_\gamma}^{\lambda 2} = \frac{A_c}{\delta C_M (\gamma' + 1 - n)} - \frac{n - \gamma'}{\gamma' + 1 - n} \varepsilon_{ML_{n-1}}^{\lambda 2}$$

The symbol n indicates the n-th complex and δ indicates the thickness of the cell. Preparation of the mixed solution must give a complex ratio γ' must between **n-1** and **n**. The following solutions were prepared for the determination of the above stability constant and absorptivity of the complex: 10.0 μg of Cu(II) with 0.200 μmol of *o*-CPF, and 10.0 μg of Fe(III) with 0.200, 0.400, 0.600 and 0.800 μmol of *o*-CPF. The measurement was at 15 °C and an ionic strength 0.01. Results are listed in Table 1. The cumulative stability constants of the Cu(*o*-CPF) and Fe(*o*-CPF)$_4$ complexes were calculated to be 7.86×10^4 and 3.36×10^{24}, respectively. The real absorptivity of the end-step complex was calculated to be 1.04×10^4 and 3.76×10^4 Lmol^{-1}cm^{-1} at 560 nm. We found

Table 1. Determination of property constants of Fe and Cu complexes with *o*-CPF at pH 6 in the presence of Triton X-100 at 15 °C and ionic strength 0.01 mol/L

n-th	Cu(*o*-CPF)		Fe(*o*-CPF)$_4$	
	stepwise K_n	stepwise absorptivity, ε_r at 560 nm	K_n	ε_r at 560 nm
1st	7.86×10^4	1.04×10^4	2.58×10^6	1.01×10^4
2nd			3.24×10^6	2.38×10^4
3rd			1.66×10^6	3.48×10^4
4th			2.42×10^5	3.76×10^4
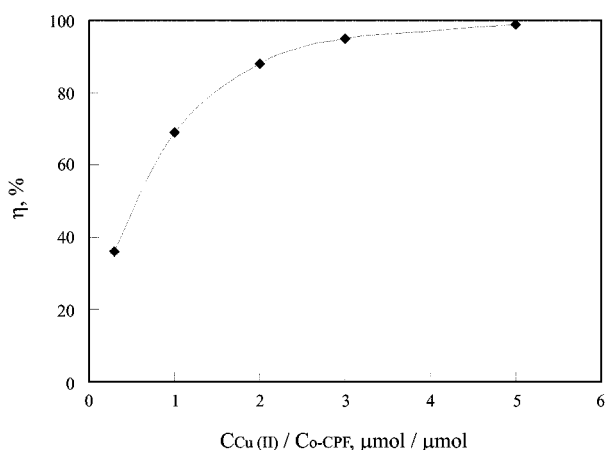
Figure 6. Effect of the molar ratio of *o*-CPF to Cu on η of *o*-CPF.

that the stability of complex Cu(*o*-CPF) was much less than that of the 1st-step complex Fe(*o*-CPF). Therefore, Fe(III) can take place of the central ion Cu from its *o*-CPF complex.

Effect of Addition of Cu and o-CPF Solutions. From Figure 6, the free *o*-CPF approaches zero when Cu molar concentration is more than three times that of *o*-CPF. When 2.0 mL of 0.05% copper sulfate was added into volumetric flask containing less than 0.08 μmol/mL *o*-CPF, this solution contained 0.08 μmol/mL Cu-*o*-CPF and much free Cu(II). The effect of 1.00 mmol/L *o*-CPF solution on absorbances of Fe-o-CPF complex much free Cu(II) is shown in Figure 7.
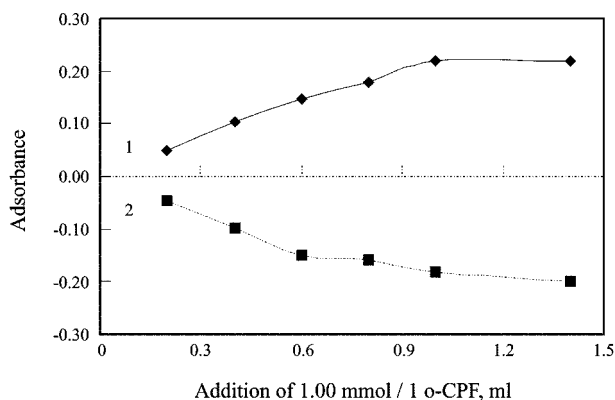
Figure 7. Effect of 1.00 mmol/L *o*-CPF in the presence of plenty of copper and 10.0 μg of Fe(III): 1- measured at 630 nm and 2- at 560 nm. both against reagent blank.
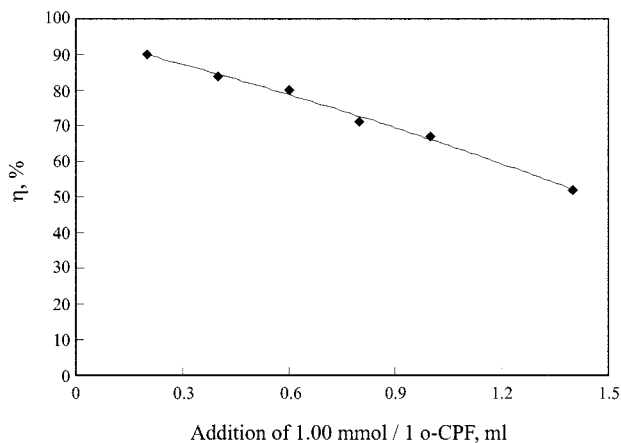
Figure 8. Effect of 1.00 mmol/L *o*-CPF on h of Cu-*o*-CPF complex.
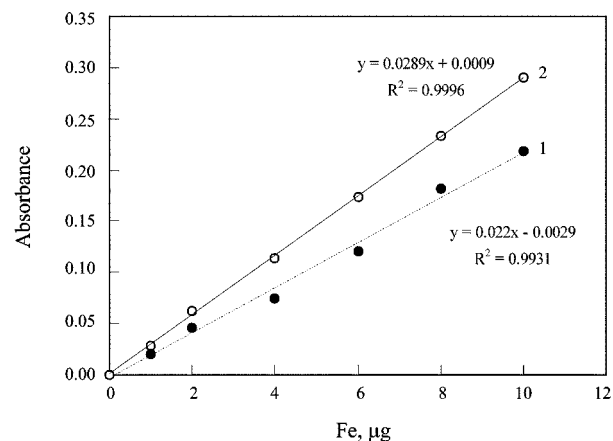
Figure 9. Calibration graphs for the determination of iron: 1- measured absorbance (ΔA) at 630 nm and 1- real absorbance (A_c).

The absorbances approach a constant when the addition of 1.00 mmol/L *o*-CPF is more than 0.8 mL. Therefore, 1.0 mL of *o*-CPF solution was used. η of the Cu-*o*-CPF complex is shown in Figure 8, and we observed that the effective fraction of Cu-*o*-CPF complex is only 67% in the solution containing 10.0 μg of Fe(III). Therefore, the excess of Cu-*o*-CPF, about 33%, will affect seriously the direct measurement of absorbance of the Fe-*o*-CPF complex. Use of the spectral correction technique in place of single wavelength spectrophotometry is necessary.

Calibration Graph. A series of standard Fe (0-10.0 μg/25 mL) solutions was prepared and the absorbance of each was measured and plotted. The absorbance curves are shown in Figure 9. Curve 1 has a higher linear slope than curve 2. All points around curve 1 are more linear than those around curve 2. Therefore, the spectral correction technique has a higher sensitivity and better accuracy that ordinary spectrophotometry.

Precision and Detection Limit. Eight replicated determinations of standard solution containing 5.00 μg of Fe(III) were carried out. The relative standard deviation (RSD) was 1.6%. However, the RSD was 11.8% by the single wave-

Table 2. Determination of total iron in samples

Sample	Added	Found	Recovery, %
River water, mg/L	0	0.066	
		0.061	
		0.061	
		0.062	
		0.069	
		0.065	
		mean. 0.064 ± 0.005	
	0.100	0.163	99.0
		0.162	98.0
		0.168	104
Coffee, mg/g	0	21.6	
		22.8	
		20.9	
		mean. 21.8 ± 1.0	
	20.0	41.3	97.5
		43.1	106
		40.7	94.5

length method. So the precision for the spectral correction technique is higher than that for ordinary spectrophotometric methods.

Using 0.010 of the real absorbance, we calculated the detection limit of iron ion to be only 0.02 mg/L.

Effect of Foreign Ions. Because Cu(II) was sufficient in the colored solution no longer containing free *o*-CPF, the addition of other metal ions did not react with o-CPF, except for Fe(III). Our experiments have shown that only Fe(II, III) and Ti(IV) can substitute Cu from the Cu-*o*-CPF complex. None of the following ions in the indicated amounts affected the direct determination of 5 μg of Fe(III) (<10% error): 10 mg of Cl^-, SO_4^{2-}, SO_3^{2-}, NO_3^-, K(I), Na(I), Be(II), Ca(II), Mg(II); 1 mg of NH_4^+, Pb(II), Mo(VI), Cr(III); 100 μg of Sn(II), Al(III),Co(II), Ni(II), Hg(II), V(V), Ge(IV), Cd(II), Mn(II) and 1 μg of Ti(IV). Therefore, the recommended method is highly selective and suitable to the determination of trace amounts of iron ion in food, beverages and water where Ti does not often exist.

Sample Analyzed. To test our method, total Fe was determined in coffee and river water. The results are given in Table 2. The recovery of standard Fe is between 94.5% and 106% and the RSD less than 5.0%.

Conclusions

We have described the basic physics of a novel approach for SCCD and applied it to several coordination systems. The complexation among *o*-CPF, Fe and Cu has further promoted this methods efficacy and advancement. This method will be used in a will survey of ongoing research into the interaction among various molecules. Not only metal ions with ligands, but also anions and organic compounds will be surveyed. The method is expected to play an important role in trace analysis due to its high selectivity.

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