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Dual-Wavelength Spectrophotometric Determination of Trace Amounts of Iron in Water and Food Using Copper-*o*-Chlorophenylfluorone Complex as Chromogenic Reagent

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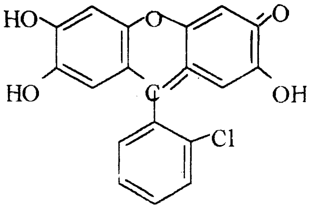
The reaction between iron (Fe^{3+}) and the chromogenic reagent, *o*-chlorophenylfluorone (*o*-CPF) was sensitive and selective at pH 6 and in the presence of excess of copper(II). It was used for the determination of trace amounts of iron by primary-secondary wavelength spectrophotometery (PSWS). This method gave higher sensitivity than ordinary spectrohotometery because it can utilize simultaneously the peak absorption and the valley absorption of the complex solution. By analyzing several samples, the relative standard deviations were less than 3.8% and the recovery rate of Fe between 92.5 and 108%.

INTRODUCTION

Iron (Fe) exists extensively in nature. Its sensitive spectrophotometric determination used the chromogenic agents: 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol[1], *o*-phenanthroline[2] etc. The synthesis of a phenylfluorone derivant, *o*-chlorophenylfluorone (*o*-CPF) was reported[3] with the following structure.



It was found to complex many metals ions between pH 3 and 7 such as titanium(IV), vanadium(V), aluminium(III), copper(II), iron(II, III), etc. Therefore, the selectivity for the determination of trace metals was poor. In this paper, we found that iron(III) had stronger complexation with *o*-CPF than other metals. It is known that iron may substitute the other metals from their *o*-CPF complexes. Hence, we established the new analytical determination of iron in food and water when excess of copper(II) exist. Copper(II) complexed *o*-CPF to form the red complex at pH 6. However, when iron co-existed, it can take the place of the complexed copper to form the blue Fe-*o*-CPF complex. The non-ionic surfactant, triton x-100 was helpful for increasing the solubility of complex. Because of the absorption interference of the excess Cu-*o*-CPF, the primary-secondary wavelength spectrophotometry (PSWS) was applied to the determination of trace amounts of iron instead of the ordinary single wavelength method. It made use of the peak absorption and the valley absorption of the reaction solution to determine metal ions so as to increase the analytical precision and accuracy. It never used the classical Lambert-Beer Law in the determinaion of components[4, 5]. Results showed that the detection limit of iron was 0.02 mg/L and the recovery rate between 92.5 and 108% accompanying with the relative standard deviation (RSD) less than 3.8%.

EXPERIMENTAL

Absorption spectra were recorded with an UV-VIS 265 spectrophotometer (Shimadzu, Japan) in 10-mm glass cells.

Standard Fe(III) solution, 100 mg/L was prepared by dissolving 0.100 g of the high-purity metal in nitric acid and diluted to 1000 mL.

Standard Fe(III) work solution, 2.00 mg/L must be 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 0.3190 g of *o*-chlorophenylfluorone (*o*-CPF, Changke Reagents of China) in 1000 mL of absolute alcohol (AR, Shanghai Reagents). It was stored in a dark bottle at *ca.* 5°C.

The buffer, pH 6.0 solution, was prepared with acetate and acetic acid so as to adjust the acidity of the complex solution.

The non-ionic surfactant solution, 1% triton x-100, was used to increase both the solubility of the complex and the sensitivity of the reaction.

Recommended Procedures

To a 25 mL volumetric flask added 2.5 mL of pH 6 buffer solution, 1 mL of 0.05% copper sulfate and 1.0 mL of *o*-CPF solution. After 10 min, the free *o*-CPF approached to zero in the reaction solution because copper(II) concentration was much higher *o*-CPF concentration in the beginning. Added a known volume of a sample solution containing less than 10.0 μg of Fe(III). Diluted to volume and mixed well. After 30 min, measured absorbances at 560 and 630 nm against a reagent blank, respectively, Calculated the factor, $\lg [(A_p + 1)/(A_s + 1)]$ value according to the following expression.

$$\lg [(A_p + 1)/(A_s + 1)] = \alpha X^{\beta}$$

where X indicated the amount of the determined component, both α and β were constant. Both A_p, A_s are the measured absorbances at the primary wavelength λ_p (peak absorption) and the secondary wavelength λ_s (valley absorption). This expression was often stable and not subject to the small variation of the operation condition.

RESULTS AND DISCUSSION

Absorption Spectra: Figure 1 shows the absorption spectra of Fe-Cu-*o*-CPF reaction solution. The peak absorption appeared at 630 nm and the valley at 560 nm. Therefore, in this study the wavelength 630 nm was selected as primary wavelength (λ_p) and 560 nm as secondary wavelength (λ_s). From the above formula, because ($A_s + 1$) value was less than 1, the use of $(A_p + 1)/(A_s + 1)$ gave higher sensitivity and better precision than that of only A_p. This method utilized the two peaks (positive and negative) of spectra, so it can decrease error to improve the analytical accuracy by eliminating the effect of the excess of Cu-*o*-CPF ligand.

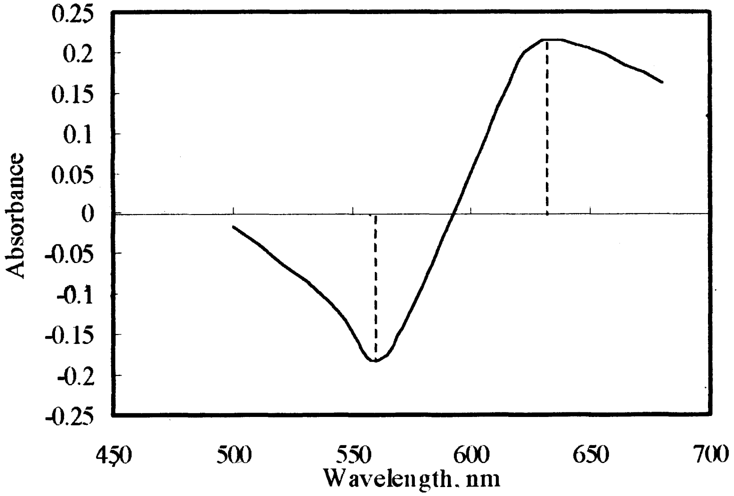


Fig. 1 Absorption spectra of Fe (10 μg)-*o*-CPF reaction solution at pH 6, against reagent blank.

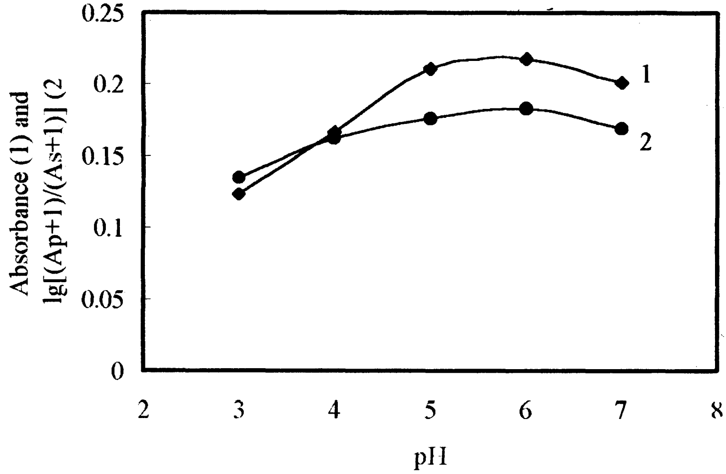


Fig. 2 Effect of pH on absorbance (curve 1 at 630 nm) and lg $[(A_p + 1)/(A_s + 1)]$ (curve 2) of Fe (10 μg)-*o*-CPF solution

Effect of pH: The effect of pH on absorbances and lg $[(A_p + 1)/(A_s + 1)]$ values is shown in Figure 2. The lg $[(A_p + 1)/(A_s + 1)]$ values approached to constant at pH between 5 and 7. In this study, pH 6 was selected. By comparing curves 1 and 2, the variation of lg $[(A_p + 1)/(A_s + 1)]$ values was less than that of absorbances. Therefore, PSWS gave out the stable coefficients α and β and not subject to the effect of the operation condition's variation.

Effect of *o*-CPF Addition: By varying the addition of *o*-CPF solution, the effects on absorbances and lg $[(A_p + 1)/(A_s + 1)]$ values were shown in Figure 3. When the addition of 1.00 mmol/L *o*-CPF was more than 0.8 mL, the term lg $[(A_p + 1)/(A_s + 1)]$ remained constant. In this work, 1.0 mL of *o*-CPF solution was added. By comparing curve 2 with 1, the variation of lg $[(A_p + 1)/(A_s + 1)]$ values was less than that of absorbances.

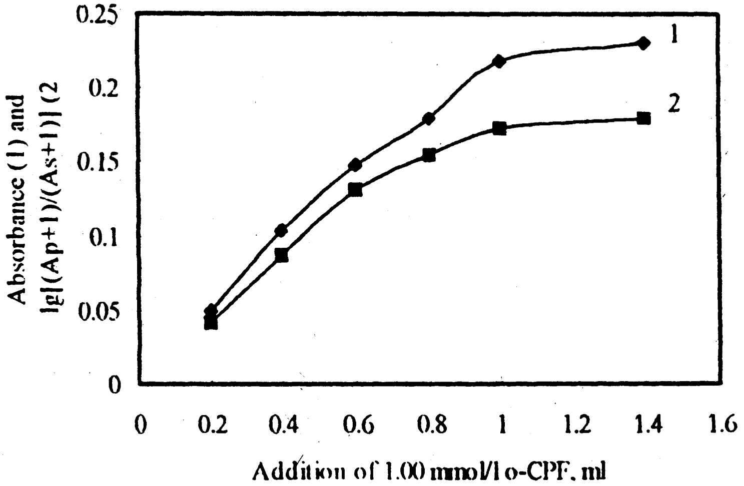


Fig. 3 Effect of 1.00 mmol/L *o*-CPF addition on absorbance (curve 1 at 630 nm) and lg $[(A_p + 1)/(A_s + 1)]$ (curve 2) of Fe (10 μg) solution

The complex ratio of Fe(III) to *o*-CPF was determined to be 1 : 4 by using β-correction spectrophotometry[6].

Effect of Time: Figure 4 shows the effect of reaction time on lg $[(A_p + 1)/(A_s + 1)]$ values of the Fe-Cu-*o*-CPF reaction solution at room temperature (15°C). It was completed in 30 min.

Calibration Graph: A series of standard Fe (X, 0–10.0 μg) solutions were prepared and the absorbance of each was measured and plotted. The lg $[(A_p + 1)/(A_s + 1)]$ value of each solution was calculated. The calibration graph is shown in Figure 5. The following expression was obtained ($\alpha = 0.0182$ and $\beta = 1$):

$$\lg [(A_p + 1)/(A_s + 1)] = 0.0182X.$$

Precision, Accuracy and Detection Limit: Eight replicate determinations of standard solution containing 2.00 μg Fe were carried out. The relative standard

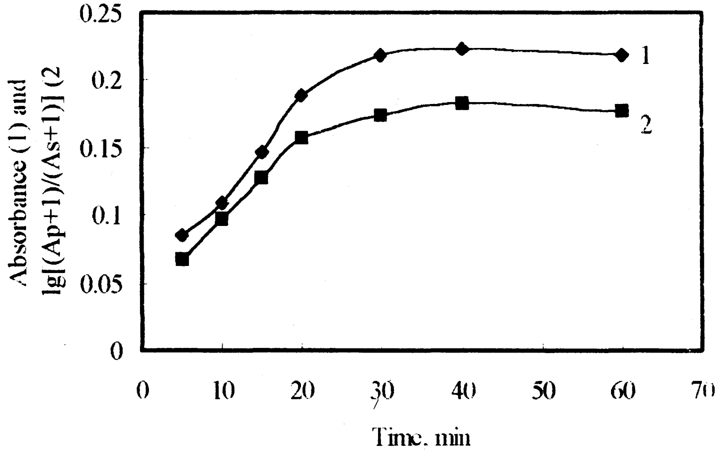


Fig. 4 Effect of the reaction time on absorbance (curve 1 at 630 nm) and lg $[(A_p + 1)/(A_s + 1)]$ (curve 2) of Fe (10 μg) solution

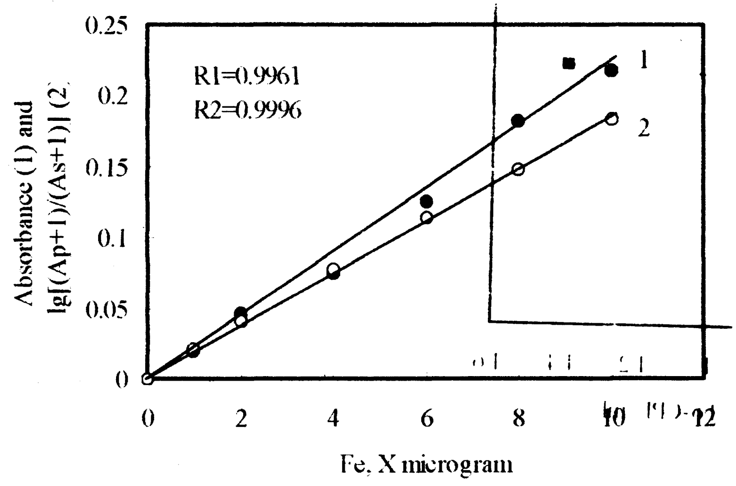


Fig. 5 Calibration graph for the determination of iron: 1. absorbance at 630 nm, and 2. lg $[(A_p + 1)/(A_s + 1)]$

deviation (RSD) was 3.5% by PSWS. However, the RSD was 9.8% by the single wavelength method. The precision for PSWS was therefore higher than that for the ordinary spectrophotometric method.

We used 0.010 of absorbance to calculate the detection limit of Fe to be 0.5 μg/25 mL (0.02 mg/L).

Effect of Foreign Ions: According to the recommended procedure, the selectivity was improved greatly because of the presence of excess of copper(II). None of the following ions will affect the direct determination of 5 μg of Fe(III) (< 10% error): 10 mg of Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, K(I), Na(I), Ti(I), Ca(II), Mg(II);

0.5 mg of F^-, PO_4^{3-}, Be(II), Pb(II), Co(II), Cd(II), Ni(II), Hg(II), Mo(VI), Cr(III), Mn(II); 0.1 mg of Al(III), V(V), Ge(IV), In(III), Sn(II); and 1 μg of Ti(IV).

Sample Analyzed

As a test of the method, total iron was determined in food and water samples. The results are listed in Table-1. The recovery of standard Fe(III) was between 92.5 and 108% and the RSD less than 3.8%.

TABLE-1
DETERMINATION OF TRACE AMOUNTS OF TOTAL IRON IN SAMPLES

Sample	Added	Found	Recovery, %
	0	0.101	
		0.103	
		0.096	
		0.098	
Water, mg/L		0.105	
		0.096	
		mean 0.100	
	0.100	0.209	104
		0.203	101
		0.199	99.5
Food, mg/g	0	7.15	
		7.24	
		7.07	
		mean 7.15	
	10.0	18.00	108
		16.40	92.5
		17.20	100

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