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Solution Properties of Aluminum and Titanium Complexes with *o*-Chlorophenylfluorone and Competition Coordination for Selective Determination of Trace Amounts of Titanium

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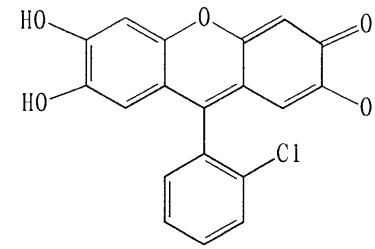
Abstract. The competition coordination for selective determination (CCSD) is described and the complexations of Ti(IV) and Al(III) with *o*-chlorophenylfluorone (*o*-CPF) is studied at pH 4.5 in presence of Triton X-100. The determination of equilibrium constants of the complexes was made by the spectral correction technique in place of ordinary spectrophotometry. The complexes are formed as $[Al(o\text{-CPF})_3]^{3-}$ and $[Ti(o\text{-CPF})_3]^{2-}$ and their stepwise and cumulative stability constants are calculated. Trace amounts of Ti can substitute Al from its *o*-CPF complex and the competition coordination has been used in the quantitative determination of Ti in water samples with satisfactory results.

Key words: Competition coordination for selective determination (CCSD); spectral correction technique; determination of Ti; *o*-Chlorophenyl-fluorone (*o*-CPF).

Tamhina and coauthors have reported several methods for the selective determination of trace amounts of Ti with tetraphenylarsonium [1], 1-phenyl-2-methyl-3-hydroxy-4-pydone [2], thiocyanate-1-phenyl-2-methyl-3-hydroxy-4-pyridone [3] and 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone [4, 5]. The reagents as 4,4-diantipyrylmethane [6], diantipyryl methane [7], dihydroxycarboxy color enol [8], rhodamine B [9] and others [10–12] were synthesized and also used in the determination of Ti. The synthesis of a phenylfluorone derivative, *o*-chlorophenylfluorone (*o*-CPF) was reported earlier [13], the structure of the compound is given below:



o-CPF

This reagent has been applied to the determination of V [14], Al [15], Ge [16] and other metals. Therefore, its selectivity is poor. The selective determination of a metal is made possible only when masking reagents were added. The novel method, the competition coordination for selective determination (CCSD) was described and it indicates the use of a metal to substitute another from its complex. The metal ions to be analyzed must have much stronger complexation with a selected ligand than most of other metals. Titanium(IV) was found to give the strongest complexation with *o*-CPF among most metals at pH 4.5. Therefore, Ti may substitute many metals from their *o*-CPF complexes except for Fe (II and III) (only in case of its high concentration). Here, Al(III) was selected in the competition coordination of Ti with *o*-CPF. At first, add enough Al(III) to the *o*-CPF solution to complex completely *o*-CPF. Then add trace amounts of titanium(IV) in order to substitute

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the combined Al and to form the new complex, Ti-*o*-CPF. The spectral correction technique was earlier established [17] and applied [16, 18–20] to the determination of the equilibrium constants of metal complexes instead of ordinary spectrophotometry. In the present work, the properties of Ti and Al complexes with *o*-CPF were determined by this method. It gives a simpler operation procedure and more acceptable principle than the classical methods *e.g.* the molar ratio, continuous variations, equilibrium movement, etc. The results show that the composition ratios of Al and Ti to *o*-CPF are both 1:3. Their cumulative stability constants are 2.68×10^{15} and 8.52×10^{16}, respectively. The competition coordination between Ti and Al with *o*-CPF has been used in the determination of Ti in samples and the recovery of Ti is between 90.0 and 109% with a relative standard deviation (RSD) of 4.0%.

Experimental

Apparatus and Reagents

Absorption spectra were recorded with a UV/VIS 265 spectrophotometer (Shimadzu, Kyoto, Japan) and the independent absorbance of solution was measured with a Model 722 (Shanghai 2ed Instruments), both with 1.0-cm cell. DDS-11A conductivity meter (Tianjin Second Analytical Instruments) was used to measure conductivity together with a DJS-1 conductivity immersion electrode (electrode constant 0.98) (Shanghai Tienkuang Devices) in the production of deionized water of 0.5–1 $\mu\Omega^{-1}$ cm^{-1}. The pH of the solution was measured with a pHS-2C acidity meter (Leici Instruments, Shanghai, China) and Model 620D pH Pen (Shanghai Ren's Electronic). The temperature was adjusted and remained constant in an electronic heated thermostat bath, Model 116R (Changjiang Test Instruments of Tongjiang, China)

Standard Ti(IV) solution, 100.0 mg/l was prepared according to the following method. Melt 0.1668 g of titanium dioxide (Shanghai Reagents) together with 3 g of potassium disulfate (Shanghai Reagents) at 700 °C in a muffle furnace. After cooling, the melt was dissolved with 5% sulfuric acid and the solution was diluted to 1000 ml with deionized water. Standard Al(III) solution, 100 mg/l was prepared by dissolving 0.100 g of high-purity Al (> 99.9%, Shanghai Chemicals) in 10 ml of 5 mol/l hydrochloric acid and diluted to 1000 ml with deionized water. Standard Ti(IV) and Al(III) working solution, both 5.00 mg/l were prepared daily by diluting the above solutions. Standard *o*-CPF solution, 1.00 mM *o*-CPF was prepared by dissolving 0.3190 g of *o*-chlorophenylfluorone (*o*-CPF, purified and provided by Changke Reagents Institute of Shanghai) in 1000 ml of absolute alcohol (A. R., Shanghai Reagents). It was stored in a dark bottle at less than 5 °C. The buffers, pH 6.0 and 4.5 solutions were prepared with acetate and acetic acid. The non-ionic surfactant solution, 1% Triton X-100 was used.

Recommended Procedures

Determination of properties of Ti and Al complexes: To a 25-ml volumetric flask add 2.5 ml of pH 6 buffer solution, 1 ml of Triton X-100 solution and a known volume of *o*-CPF solution. Add 10.0 µg of Ti(IV) or 10.0 µg of Al(III). Dilute to volume and mix well. After 20 min, measure absorbances at 475 (λ_1) and 575 nm ($\lambda_{2\text{-Ti}}$) (Ti-*o*-CPF solution) or 475 (λ_1) and 555 nm ($\lambda_{2\text{-Al}}$) (Al-*o*-CPF solution) against a reagent blank, respectively. Calculate the real absorbance (A_c) of the complexes by the relation [17]:

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha\beta} \quad \text{where} \quad \alpha = \frac{\varepsilon_{ML_\gamma}^{\lambda_1}}{\varepsilon_{ML_\gamma}^{\lambda_2}} \quad \text{and} \quad \beta = \frac{\varepsilon_L^{\lambda 2}}{\varepsilon_L^{\lambda 1}}$$

Here, the symbols ΔA and $\Delta A'$ are the absorbances of the *M* (metal) $-L$ (ligand) solution against the *L* solution without Al or Ti, respectively, measured at the peak wavelengths (λ_2) and the valley wavelength (λ_1). The correction coefficients α and β are 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 absorptivities of the complex (ML_γ) solution without free *L* and the *L* solution without *M* against water reference, respectively, measured at λ_1 and λ_2.

Determination of trace amounts of titanium: To a 25-ml volumetric flask, add 2.5 ml of pH 4.5 buffer solution, 1 ml of Triton X-100 solution, 2 ml of 0.05% aluminum sulfate and 1.0 ml of the *o*-CPF solution. After 10 min, the free *o*-CPF approaches to zero in the reaction solution because the aluminum(III) concentration is much higher than the *o*-CPF concentration at the beginning. Add a known volume of a sample solution containing less than 10.0 µg of Ti(IV). Dilute to volume and mix well. Place it into a warm water bath at constant temperature 40 °C for 3 min and then measure it after cooling to room temperature at 495 and 580 nm against a reagent blank without Ti, respectively. Calculate the real absorbance (A_c) of the Ti-*o*-CPF complex by means of the expression above.

Results and Discussion

Analysis of Absorption Spectra

Figure 1 shows the absorption spectra of *o*-CPF and its Ti(IV) and Al(III) complex solutions at pH 6.0. We observe that their peak absorptions are located at 500, 580 and 540 nm, respectively. So, the red shift of the spectral peak of the Ti-*o*-CPF complex is 80 nm and that of the Al-*o*-CPF only 40 nm. Because of the little wavelengths difference and the negligible absorption of excess of *o*-CPF at the working wavelength (λ_2), the single wavelength spectrophotometry is not suitable in this work. However, from the relative spectrum 2 of the Al-*o*-CPF solution, the peak absorption is located at 555 nm and the valley absorption at 500 nm. Similarly, from curve 3, the peak absorption is located at 575 nm and the valley absorption at 475 nm. In order to obtain the maximal absorbance and minimal error in measurement of the solutions, the working wavelengths 475 and 555 nm and 475 and 575 nm may be used in the determination of equilibrium constants of Al and Ti complexes: $\beta_{1\text{-}o\text{-CPF}}$ calculated to be 0.246 (555 nm/475 nm), $\beta_{2\text{-}o\text{-CPF}}$ to be 0.069 (575 nm/475 nm) both from curve 1, $\alpha_{\text{Al-}o\text{-CPF}}$ to be

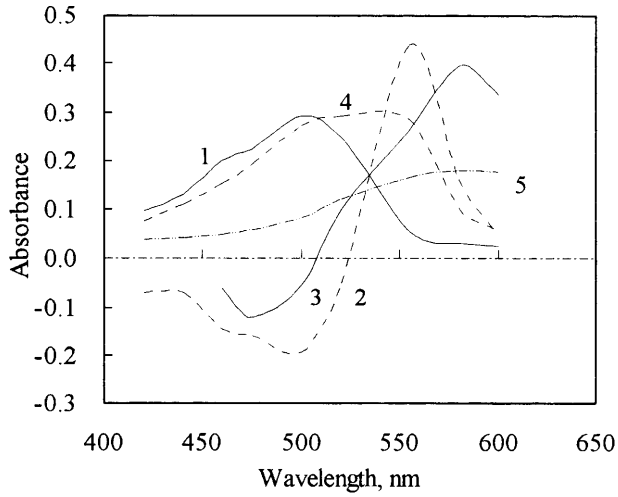

Fig. 1. Absorption spectra of the *o*-CPF and its Al and Ti solutions at pH 6 in presence of triton x-100: 1 – *o*-CPF (0.500 μmol), 2 – Al(III) (10.0 μg) – *o*-CPF(1.50 μmol) solution, 3 – Ti(IV) (10.0 μg) – *o*-CPF(1.50 μmol) solution, 4 – Al(III) (200 μg) – *o*-CPF (0.50 μmol) complex solution (no longer containing free *o*-CPF), 5 – Ti(IV) (100 μg) – *o*-CPF (0.10 μmol) complex solution (no longer containing free *o*-CPF). 1, 4 and 5 all against water reference and the others against reagent blank without Al and Ti

0.675 (475 nm/555 nm) from curve 4 and $\alpha_{\text{Ti-}o\text{-CPF}}$ to be 0.328 (475 nm/575 nm) from curve 5. Therefore, the following relations were used to calculate the real absorbance of the Al-*o*-CPF complex at 555 nm and that of Ti-*o*-CPF complex at 575 nm: $A_{c/\text{Al-}o\text{-CPF}} = 1.20(\Delta A\text{-}0.246\Delta A')$ and $A_{c/\text{Ti-}o\text{-CPF}} = 1.02(\Delta A\text{-}0.069\Delta A')$, respectively.

Effect of o-CPF Concentration

The effect of molar concentration of the *o*-CPF solution on absorbances of the Ti(IV)-*o*-CPF and Al(III)-*o*-CPF solutions is shown in Fig. 2. From curves 2 and 5, it is difficult for the complex ratio of *o*-CPF to Ti and Al to be calculated accurately with the molar ratio method because their inflexion points cannot be observed accurately and precisely by comparing curves 2 with 3 and 5 with 6, the real absorbance (A_c) of the complexes is always higher than the measured absorbance of the solutions. The absorbance difference between curve 2 and 3 and between 5 and 6 was neglected in ordinary spectrophotometry but it was used in the calculation of the equilibrium constants of the complexes in the recommended method. The fraction (η%) of the effective *o*-CPF and its molar ratio (γ') to Ti or Al can be calculated by the relations:

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

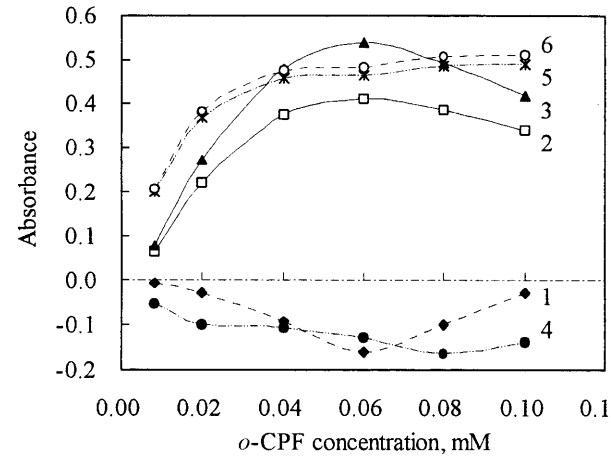

Fig. 2. Effect of molar concentration of *o*-CPF on absorption of the solution at pH 6 in presence of Triton X-100: 1 – absorbance of the Al (10.0 μg) – *o*-CPF solution measured at 475 nm, 2 – same as 1 but at 555 nm, 3 – real absorbance of the Al (10.0 μg) – *o*-CPF complex at 555 nm, 4 – absorbance of the Ti (10.0 μg) – *o*-CPF solution measured at 475 nm, 5 – same as 1 but at 575 nm, 6 – real absorbance of the Ti (10.0 μg) – *o*-CPF complex at 575 nm

The symbols, $\mathbf{C_M}$ and $\mathbf{C_L}$ indicate the molar concentrations of Ti or Al and *o*-CPF at the beginning, respectively. $\mathbf{A_o}$ is the absorbance of the *o*-CPF solution against water at λ_2. From curves in Fig. 4, γ' of *o*-CPF to Al and that of *o*-CPF to Ti both approach 3 when *o*-CPF is more than 0.04 mM. Therefore, the complexes $[\text{Al}(o\text{-CPF})_3]^{3-}$ and $[\text{Ti}(o\text{-CPF})_3]^{2-}$ were formed here. From the curves in Fig. 3, we observe that η of *o*-CPF is about 78% in the Al(10 μg)-*o*-CPF solution and only 40% in the Ti(10 μg)-*o*-CPF solution at the addition of 1.5 ml of the *o*-CPF solution. The

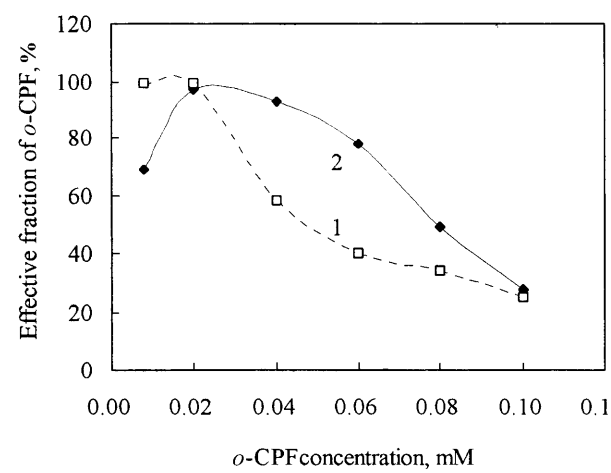

Fig. 3. Effect of molar concentration of *o*-CPF on the fraction (η%) of the effective *o*-CPF in solutions still containing: 1 – Al(III) (10.0 μg) and 2 – Ti(IV) (10.0 μg)

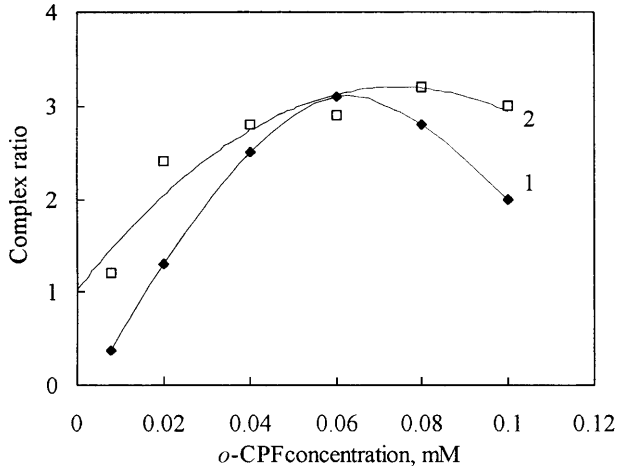

Fig. 4. Effect of molar concentration of *o*-CPF on the complex ratio(γ') of *o*-CPF to: 1 – Al(III) (10.0 μg) and 2 – Ti(IV) (10.0 μg)

excess of *o*-CPF is 22% and 60%, respectively. It is inevitable for so much free *o*-CPF to affect the accurate measurement of absorbance of the complex.

Effect of pH and Reaction Time

By varying the pH of the solution, the absorbance curve is shown in Fig. 5. The absorption of the Ti-*o*-CPF solution approaches constant when pH is between 4 and 7, but the Al-*o*-CPF solution shows a peak between pH 6 and 7. In the determination of

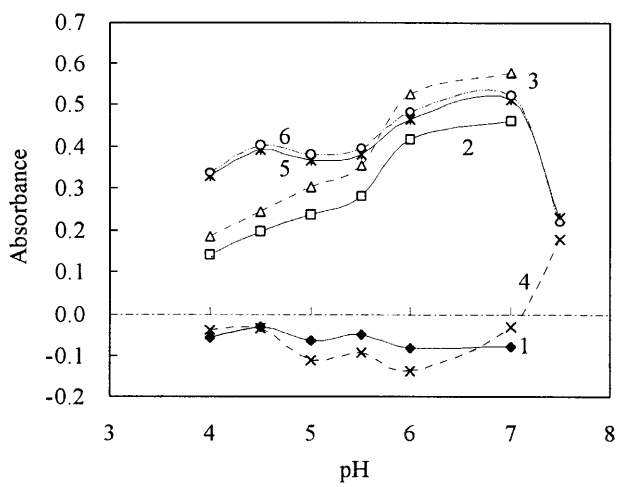

Fig. 5. Effect of pH on absorption of the solutions in the presence of Triton X-100: 1 – absorbance of the Al (10.0 μg) – *o*-CPF (1.00 μmol) solution measured at 475 nm, 2 – same as 1 but at 555 nm, 3 – real absorbance of the Al (10.0 μg) – *o*-CPF(1.00 μmol) complex at 555 nm, 4 – absorbance of the Ti (10.0 μg) – *o*-CPF (1.00 μmol) solution measured at 475 nm, 5 – same as 1 but at 575 nm, 6 – real absorbance of the Ti (10.0 μg) – *o*-CPF(1.00 μmol) complex at 575 nm

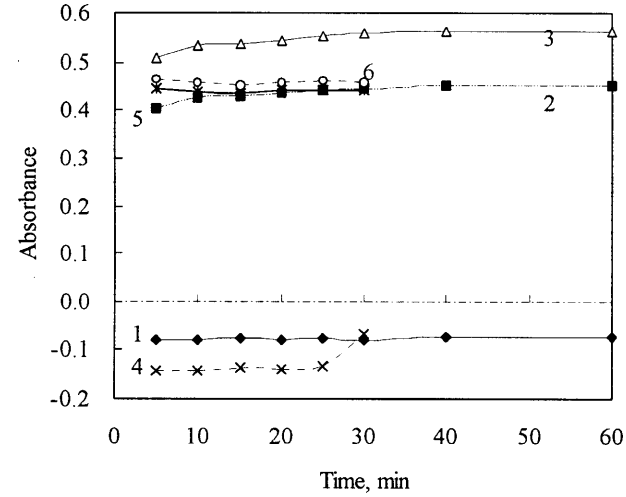

Fig. 6. Effect of the reaction time on absorption of solutions at pH 6 in the presence of Triton X-100: 1 – absorbance of the Al (10.0 μg) – *o*-CPF (1.00 μmol) solution measured at 475 nm, 2 – same as 1 but at 555 nm, 3 – real absorbance of the Al (10.0 μg) – *o*-CPF(1.00 μmol) complex at 555 nm, 4 – absorbance of the Ti (10.0 μg) – *o*-CPF(1.00 μmol) solution measured at 475 nm, 5 – same as 1 but at 575 nm, 6 – real absorbance of the Ti (10.0 μg) – *o*-CPF(1.00 μmol) complex at 575 nm

equilibrium constants of the Al-*o*-CPF and Ti-*o*-CPF complexes, pH 6.0 buffer solution was added. The effect of the reaction time is shown in Fig. 6. The reaction between Al and *o*-CPF is complete in 20 min and that between Ti and *o*-CPF only in 5 min. We observed that the absorbance of the solutions remains constant for at least 2 hours.

Determination of Stability Constant and Absorptivity of Complexes

The stepwise stability constant (K_n), cumulative constant (K) and stepwise absorptivity (ε) of a complex can be calculated by means of:

$$K_n = \frac{\gamma' + 1 - n}{(n - \gamma')(C_L - \gamma' C_M)}$$

and the cumulative constant(K) $K = \prod_{n=1}^{\gamma} K_n$

$$\varepsilon_{ML_n}^{\lambda_2} = \frac{A_c}{\delta C_M(\gamma' + 1 - n)} - \frac{n - \gamma'}{\gamma' + 1 - n}\varepsilon_{ML_{n-1}}^{\lambda_2}$$

The symbol n indicates the step number of the complex and δ the thickness of the cell. The molar ratio γ' of the effective L to M in solution is between $n - 1$ and n. The following solutions were prepared: 10.0 μg of Al(III) with 0.250 μmol of *o*-CPF, 3.00 μg

Table 1. Determination of equilibrium constants and molar absorptivity of the Ti and Al complexes with *o*-CPF at pH 6 in the presence of Triton x-100 at 15 °C and ion strength 0.01 M

n-th	Al(*o*-CPF)$_3$		Ti(*o*-CPF)$_3$	
	step K_n	Step absorptivity, ε_r at 555 nm	K_n	ε_r at 575 nm
1st	3.08×10^5	1.35×10^4	7.82×10^5	2.18×10^4
2nd	1.21×10^5	2.70×10^4	6.99×10^5	4.42×10^4
3rd	7.19×10^4	4.01×10^4	1.56×10^5	6.44×10^4

of Al(III) with 0.200 µmol of *o*-CPF, 4.00 µg of Al(III) with 0.400 µmol of *o*-CPF, 5.00 µg of Ti(IV) with 0.100 µmol of *o*-CPF, 2.00 µg of Ti(IV) with 0.100 µmol of *o*-CPF and 10.00 µg of Ti(IV) with 0.900 µmol of *o*-CPF. The measurement temperature was 15 °C and the ionic strength 0.01 M. Three replicate determinations of each solution were carried out and the results are given in Table 1. The cumulative stability constants of the $[\mathrm{Al}(o\text{-CPF})_3]^{3-}$ and $[\mathrm{Ti}(o\text{-CPF})_3]^{2-}$ complexes are 2.68×10^{15} and 8.52×10^{16}, respectively. We observed that the stability constant of the complex $[\mathrm{Al}(o\text{-CPF})_3]^{3-}$ is only one-thirty that of complex $[\mathrm{Ti}(o\text{-CPF})_3]^{2-}$. Therefore, Ti(IV) can substitute Al from the Al-*o*-CPF complex. By observing the real absorptivity of the complexes shown in Table 1, the reactions between Al and *o*-CPF and between Ti and *o*-CPF are sensitive.

Substitution Coordination and Determination of Ti

Effect of Operation Conditions. Once Ti(IV) was added into the Al-*o*-CPF complex solution, the following was observed: the solution began to change into orange (*o*-CPF color) from red (Al-*o*-CPF color) and then rapidly changed into blue (Ti-*o*-CPF color). So, the substitution process between Ti(IV) and Al-*o*-CPF complex at pH 4.5 in the presence of Triton X-100 can be expressed as:

$$\mathrm{Al(III)} + o\text{-CPF} \rightarrow [\mathrm{Al}(o\text{-CPF})]^+$$
(at the beginning when an excess of aluminum exists)

$$\mathrm{Ti(IV)} + [\mathrm{Al}(o\text{-CPF})]^+ \rightarrow \mathrm{Al(III)} + \mathrm{Ti(IV)} + o\text{-CPF}$$
(rapid transition)

$$\mathrm{Ti(IV)} + 3\ o\text{-CPF} \rightarrow [\mathrm{Ti}(o\text{-CPF})_3]^{2-}$$
(at equilibrium)

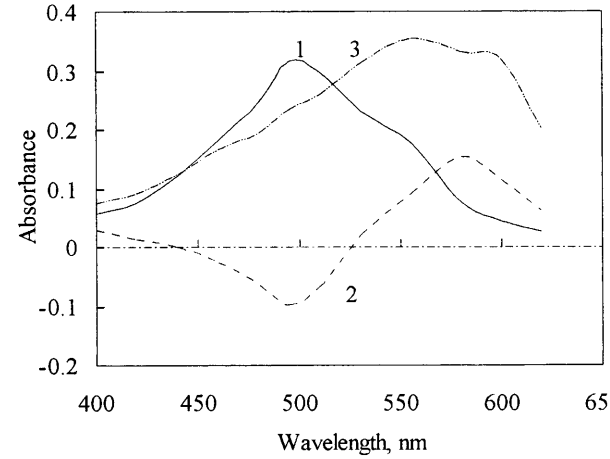

Fig. 7. Absorption spectra of the Al-*o*-CPF complex and its Ti mixed solution at pH 4.5 in presence of triton x-100: 1 – Al(III) (200 µg) – *o*-CPF (0.50 µmol) complex (no longer containing free *o*-CPF), 2 – Ti(IV) (10.0 µg)–Al(III) (200 µg) – *o*-CPF (0.50 µmol) mixed solution, 2 – Ti(IV) (100 µg) – *o*-CPF (0.100 µmol) complex (no longer containing free *o*-CPF and Al-*o*-CPF complex). 1 – and 3 – both against water reference and 22 against reagent blank without Ti

Figure 7 shows the absorption spectra of the solutions. From curve 2, we select both 495 and 580 nm as the working wavelengths in presence of an excess of Al(III) because of the valley and peak absorption. The correction coefficient $\beta_{\text{Al-}o\text{-CPF}}$ is 0.240 (580 nm/495 nm) from curve 1 and $\alpha_{\text{Ti-}o\text{-CPF}}$ is 0.705 (495 nm/580 nm) from curve 3. The real absorbance (A_c) of the Ti-*o*-CPF complex at 580 nm was calculated by the relation: $A_c = 1.20(\Delta A - 0.240\Delta A')$.

Figure 8 gives the effect of pH on the absorption of the Ti-Al-*o*-CPF mixed solution. From curves 2 and 3, the measured absorbance of the solution and real absorbance (A_c) of the Ti-*o*-CPF complex both reach a maximum at pH 4.5. The effect of the reaction time is shown in Fig. 9. We observed that the substitution reaction is very slow at room temperature but it becomes very rapid at 40 °C. We observed that floccules appeared when the time was more than 10 min. Therefore, it was suggested that the reaction solution was kept in 40 °C warm water for 3 min and then to measure it after cooled to room temperature. Experimental result has shown that the free *o*-CPF approaches zero when the molar concentration of Al(III) was more than six times that of *o*-CPF. Therefore, an aluminum amount, being seven times the concentration of *o*-CPF is always added to complex *o*-CPF completely. The effect of the addition of the

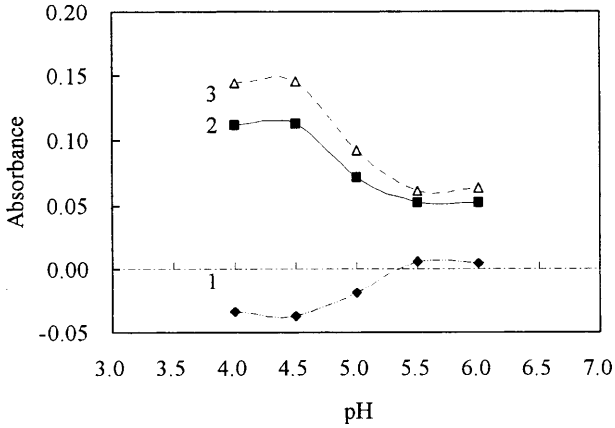

Fig. 8. Effect of pH on the determination of Ti using the Al-*o*-CPF complex as chromogenic agent: 1 – Ti (10.0 μg)-Al (200 μg) – *o*-CPF (0.500 μmol) solution at 495 nm, 2 – same as 1 but at 580 nm, 3 – real absorbance of the Ti (10.0 μg)-*o*-CPF(0.500 μmol) complex at 580 nm

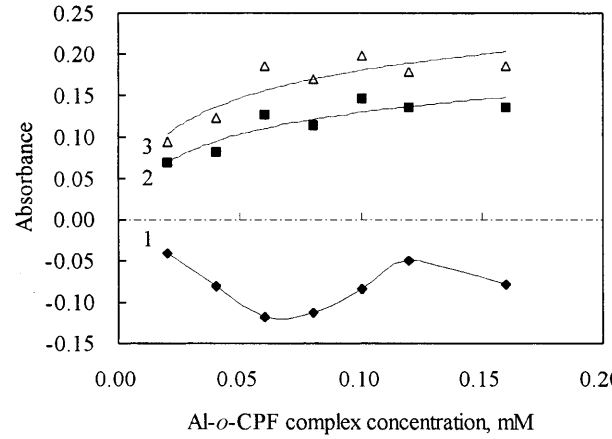

Fig. 10. Effect of the Al-*o*-CPF complex concentration on the absorption of the Ti-*o*-CPF complex at pH 4.5: 1 – Ti (10.0 μg)-Al (six times the molar concentration of *o*-CPF)-*o*-CPF solution at 495 nm, 2 – same as 1 but at 580 nm, 3 – real absorbance of the Ti (10.0 μg)-*o*-CPF complex at 580 nm

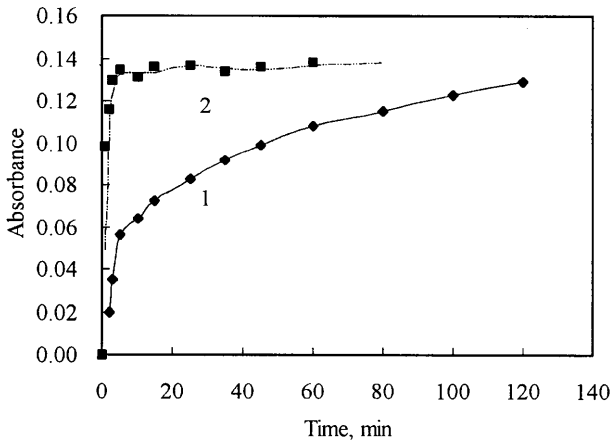

Fig. 9. Effect of the reaction time on the determination of Ti at pH 4.5: 1-Ti (10.0 μg)-Al (200 μg)-*o*-CPF (0.500 μmol) solution at room temperature (20 °C), 2 – same as 1 – but the solution was kept in 40 °C warm water bath for 3 min then cooled. Both at 580 nm, against reagent blank reference

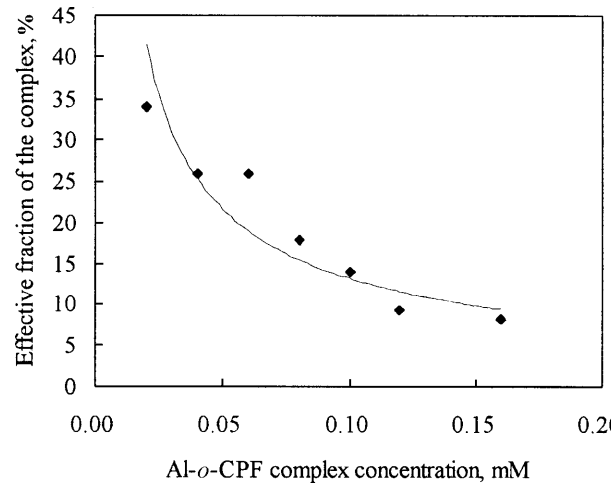

Fig. 11. Effect of molar concentration of *o*-CPF on the fraction (η%) of the effective Al-*o*-CPF complex at pH 4.5

o-CPF solution on the absorption of the Ti-Al-*o*-CPF solution is shown in Fig. 10. From curves 1 and 2 in Fig. 10, we observe that the absorption approaches constant when the addition of the *o*-CPF solution is between 1.5 and 4.0 ml. Therefore, the addition of 2.5 ml of the *o*-CPF solution is suggested in the determination of trace amounts of Ti. The fraction (η%) of the effective Al-*o*-CPF complex is calculated as shown in Fig. 11. We observe that only 14% of the Al-*o*-CPF complex is useful and 86% of the Al-*o*-CPF complex still remains free in the substitution solution at the addition of 2.5 ml of the *o*-CPF solution. Therefore, such an excess of the Al-*o*-CPF complex affects seriously the direct measurement of the absorbance of the Ti-*o*-CPF complex and the single wavelength spectrophotometry is not suitable to the substitution reaction. It is advantageous for the quantitative determination of trace amounts of Ti to use the spectral correction technique instead of the single wavelength spectrophotometry.

Standard Curves. A series of standard Ti (0–10.0 μg) solutions were prepared and the absorbance of each was measured and plotted. The curves and regression equations are shown in Fig. 12. In the range

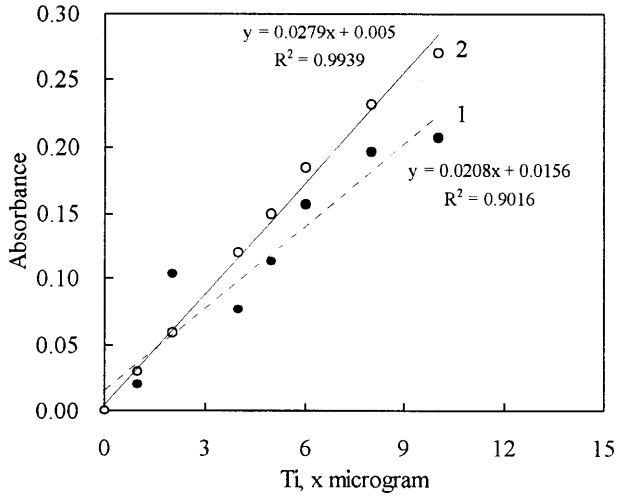

Fig. 12. Calibration graph for the determination of Ti at pH 4.5 in the presence of Triton X-100: 1 – absorbance (ΔA) measured at 580 nm and 2 – real absorbance (A_c)

between 0 and 10.0 µg of Ti, the A_c points around curve 2 are more linear than the ΔA points around curve 1. Therefore, the spectral correction technique has higher sensitivity and better accuracy than single wavelength spectrophotometry.

Precision, Accuracy and Detection Limit. Six replicate determinations of the standard solution containing 5.00 µg of Ti(IV) were made. The average is 4.96 ± 0.17 µg and the RSD 3.4%. However, the average is 4.24 ± 0.67 µg and the RSD 15.9% by the single wavelength spectrophotometry. As a result, the accuracy and precision of the spectral correction technique are higher than those of single wavelength spectrophotometry. Use $A_c = 0.010$ to calculate the detection limit of Ti to be 0.3 µg/25 ml (0.01 mg/l).

Selectivity of Method. Because Al concentration is very high and the free *o*-CPF approaches zero, the other metals cannot be complexed with *o*-CPF. Experimental results have shown that most metals can not substitute Al from the Al-*o*-CPF complex except Ti(IV). Therefore, the recommended method is highly selective. Despite the absence of any masking reagent, none of the following ions will affect the direct determination of 5 µg of Ti(IV) (<10% error): 10 mg of Cl^-, SO_4^{2-}, SO_3^{2-}, 1 mg of Be(II), Ca(II), Mg(II), 0.4 mg of Cd(II), 0.2 mg of Cu(II), W(III), Co(II), Ni(II), Hg(II), Zn(II), 0.12 mg of Mn(II), 0.04 mg of V(V), Mo(VI) and 0.01 mg of Fe(II, III).

Sample Analyzed. As a test of the method, total titanium was determined in water samples. The results are given in Table 2. The recovery of Ti(IV) is between 90.0 and 109% and the RSD 4.0%.

Table 2. Determination of titanium in water samples

Sample	Added, mg/l	Found, mg/l	Recovery, %
River water	0	<0.01	
		<0.01	
		<0.01	
		mean. <0.01	
	0.080	0.081	101
		0.072	90.0
Synthetic sample	0	0.078	
		0.073	
		0.077	
		0.081	
		0.081	
		0.080	
		mean. 0.078	
		RSD. 4.0%	
	0.200	0.297	109
		0.293	107
		0.288	105
Underground water	0	0.126	
		0.111	
		0.139	
		mean. 0.125	
	0.100	0.196	90.0
		0.212	109
		0.197	90.0

Conclusion

The spectral correction technique is one of the dual-wavelength spectrophotometric methods but different from the others [21–23] in operation. Not only does it give the accurate determination of trace amounts of a metal (*M*) but also the calculation of equilibrium constants of a complex is obtained easily. The current chromogenic reagent (*L*) itself often has very high molar absorptivity and its absorption occupies a great and assignable fraction. Just the assignable excess of *L* controls strictly the dynamic equilibrium between *M* and *L*. The spectral correction technique may give the absorbance fraction of each color compound or ion co-existing in the mixed solution, so the composition ratio and formation constant of the complex may be calculated accurately by this technique. The competition coordination reaction is often applied in analytical compleometry *e.g.* complexometric titration. The spectral correction technique makes the competition coordination more suitable to spectrophotometry with high selectivity. Surely, the combination of the CCSD and the spectral correction technique will play an important role in the study of the selective spectrophotometric determination of metal ions.

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