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A Spectrophotometric Study of Indoferron as a Color Reagent for Zirconium(IV) and Iron(III)*1

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Indoferron is shown to be a useful spectrophotometric reagent for the determination of zirconium(IV) and iron(III). An excess reagent reacts with zirconium(IV) and iron(III) to form blue complexes, which have absorption maxima at 605 and 590 mμ respectively against the reagent blank. The maximum absorbances of the solutions containing the complexes are obtained in the pH range from 3.6 to 3.7 for zirconium(IV), and in that from 3.9 to 4.1 for iron(III). The former complex is stable for 1 hr, and the latter, for 4 hrs. The color systems obey Beer's law in 25 m*l* over the ranges up to 40 μg Zr and up to 50 μg Fe respectively. The molar absorptivities of the complexes are calculated to be 3.18×10^4 for zirconium(IV) and 1.81×10^4 for iron(III). The sensitivities of the reactions are 0.0038 μg Zr/cm^2 and 0.0039 μg Fe/cm^2 for an absorbance of 0.001. As for composition, the complexes used have a metal-to-ligand ratio of 1:3 for zirconium(IV) and 1:2 for iron(III). The apparent formation constant of the complex for iron(III) is calculated to be $7.81\times 10.^{10}$

Indoferron [2,6-dibromo-3′-methyl-5′-*N*,*N*-di(carboxymethyl)aminomethyl-indophenol] was prepared by Körbl *et al.*[1] as a chromogenic dye-stuff. They studied the complex formation between this reagent and such metal cations as bismuth(III), thorium(IV), scandium(III), and iron(III), and discussed the molar absorptivities of the complexes thus formed. Recently, the spectrophotometric determination of scandium(III) with the reagent has been described by Shimizu and Ogami.[2]

A preliminary investigation was undertaken to evaluate the usefulness of indoferron as a spectrophotometric reagent for various metal cations: bismuth(III), thorium(IV), iron(III), zirconium(IV), vanadium(IV), gallium(III), indium(III), and copper(II). The reagent reacts with those metal cations in a slightly acidic medium (~pH 5.5) to form colored complexes. The results show that indoferron may be useful as a color reagent for the spectrophotometric determination of these metal cations; in every case, the chelation occurs instantaneously at room temperature; all the complexes formed are water-soluble; and their molar absorptivities are of the order of 10^4.

This paper will describe the fundamental conditions for the spectrophotometric determinations of zirconium(IV) and iron(III). Indoferron is not a very good reagent for these elements, but the properties of these complexes are worth being analysed.

Experimental

Reagents and Apparatus. *Indoferron* (abbreviated IF; MW, 560.12 as Na$_2$ salt) *Solution.* A 1×10^{-3}M IF solution was prepared by dissolving the Dotite IF reagent in water; fresh solutions were used for each set of experiments.

Zirconium(IV) Solution. A 1×10^{-2}M zirconium(IV) solution was prepared by dissolving a guaranteed zirconyl nitrate dihydrate in about 2N perchloric acid. The solution was standardized by EDTA titration, using xylenol orange as the indicator.[3]

Iron(III) Solution. About a 1×10^{-2}M iron(III) solution was prepared by dissolving purified iron(III) hydroxide in 1N perchloric acid. The solution was standardized by EDTA titration, using Cu-PAN as the indicator.[4]

Stock solutions of diverse ions were prepared from their reagent-grade chemicals in appropriate concentrations.

A 0.25 or 2M acetic acid - sodium acetate buffer solution was used for the pH adjustment.

A Hitachi recording spectrophotometer with 1-cm cells, Model 124, was used for the absorbance measurements. A Hitachi-Horiba glass-electrode pH meter,

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[1] J. Körbl and V. Svoboda, *Chem. Ind.* (London), **1958**, 1233: V. Svoboda, L. Dorazil and J. Körbl, *Collection Czech. Chem. Commun.*, **25**, 1037 (1960).

[2] T. Shimizu and K. Ogami, *Talanta*, **16**, 1527 (1969).

[3] K. Ueno, "Kireto Tekitei (Chelatometric Titration)" (in Japanese), Nankodo, Tokyo (1960), p. 325.

[4] *Idem, ibid.*, p. 256.

Model M-5, was used for the pH measurments.

All the measurements were made at 25±0.5°C.

Results and Discussion

Absorption Curves. *Indoferron.* Measurements were made as a function of the pH. As is shown in Fig. 1, below pH 4, the solution has an absorption maximum at about 485 mμ. Between pH 5 and 9, however, the solution has an absorption maximum at about 617 mμ. Above pH 9, this absorption maximum shifts towards a lower wavelength; it is at 580 mμ in the pH range from 11 to 14.

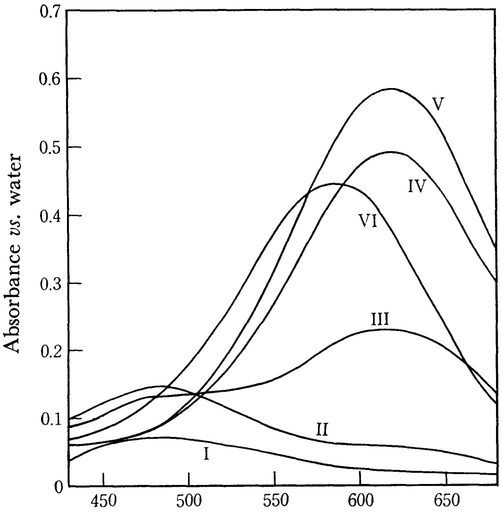

Fig. 1. Absorption curves of IF.
IF: 4.0×10^{-5}M, μ=01, pH—I: 2.0, II: 4.0, III: 4.9, IV: 6.1, V: 9.0, VI: 11—14.

Some Metal-IF Complexes. An attempt was made to evaluate the usefulness of indoferron as a spectrophotometric reagent for several metal cations. To a solution containing a 2.0×10^{-5}M (finally) metal cation in a 25-m*l* volumetric flask, we added 2 m*l* of a 1×10^{-3}M IF solution and 10 m*l* of a 0.25M acetate buffer solution adjusted in the pH range from 2.0 to 5.5 (at intervals of 0.5). The solution was then diluted to the mark with water. The absorbances of the colored complexes were measured against the reagent blanks. The data thus obtained are summarized in Table 1.

Zirconium(IV)-IF Complex. A colored solution containing 23.0 μg of zirconium(IV) was measured in the same way. In this case, 10-m*l* portions of a 2M acetate buffer solution adjusted to various pHs were used. As Fig. 2 shows, the maximum absorption is found at 625 mμ below pH 2.5, at 605 mμ between pH 3 and 3.5, and at 590 mμ at pH 4.5. From the viewpoint of the sensitivity of the reaction, the complex with its absorption maximum at about 605 mμ was used for the determination of zirconium(IV).

Table 1. Properties of metal-indoferron complexes

Metal Cations: each 2.0×10^{-5}M,
IF: 8.0×10^{-5}M, μ=0.1

Metal	pH	λ^*_{max} mμ	M: L**	ε^{***} $\times10^{-4}$	Color
Th(IV)	3.0	615	1 : 2	1.75	Blue
	4.0	648	1 : 3	3.95	Blue-green
V(IV)	3.5	603	1 : 2	1.85	Blue
Bi(III)	3.0	575	1 : 2	1.01	Purple
Ga(III)	3.0	585	1 : 2	1.29	Blue
In(III)	4.0	605	1 : 2	1.57	Blue
Cu(III)	5.5	670	1 : 2	1.74	Blue-green
Sc(III)[2]	4.1	600	1 : 2	0.96	

* Wavelength of maximum absorbance
** Composition of the complex measured by the method of continuous variation
*** Molar absorptivity of the complex

Iron(III)-IF Complex. A colored solution containing 32.2 μg of iron(III) was measured in a manner similar to that used for the zirconium. In this case, 1 m*l* of a 1×10^{-3}M IF solution and 10 m*l* of a 0.25M acetate buffer solution were used. The curves were characterized by an absorption maximum at 590 mμ in the pH range from 2.5 to 4.5. Some of the results are shown in Fig. 3.

The Effect of pH. The absorbances of the solutions containing the complexes were measured

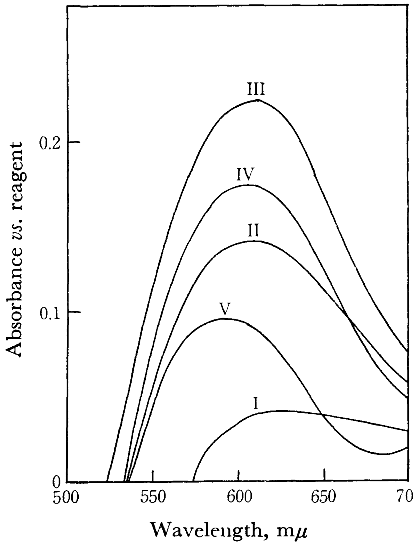

Fig. 2. Absorption curves of the solution containing complex in the presence of an excess of reagent over zirconium.
Zr: 23.0 μg (1.00×10^{-5}M), IF: 8.00×10^{-5}M, pH—I: 2.50, II: 3.00, III: 3.50, IV: 4.00, V: 4.50, μ=1.44.

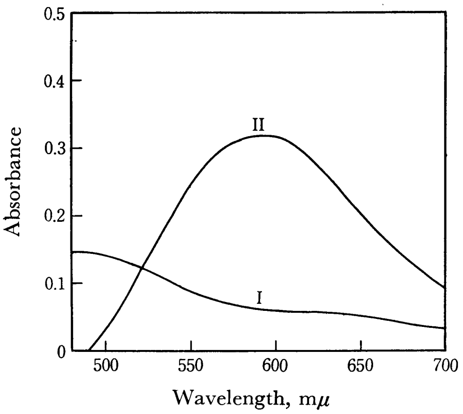

Fig. 3. Absorption curves of IF and its iron complex in the presence of an excess of reagent.
Fe(III): 32.2 μg (2.31×10^{-5}M), IF: 4.00×10^{-5}M
I: IF *vs.* water
II: Fe(III)—IF complex *vs.* reagent
μ: 0.1, pH 4.0.

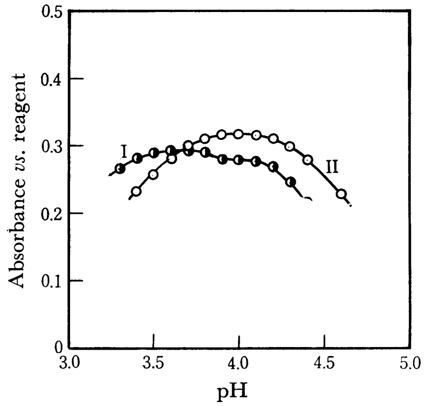

Fig. 4. Effect of pH.
I: Zr(IV); 25.1 μg, IF; 6.06×10^{-5}M, 605 mμ, μ; 1.44
II: Fe(III); 32.2 μg, IF; 4.00×10^{-5}M, 590 mμ, μ; 0.1

as a function of the pH. The ranges in which the highest absorbance was obtained were found to be pH 3.6—3.7 for zirconium(IV) and pH 3.9—4.1 for iron(III) (Fig. 4).

The Effect of the Reagent Concentration. A volume of 1.9—2.0 m*l* of a 1×10^{-3}M IF solution suffices for the complete development of color with less than 40 μg of zirconium, while 1.5—2.1 m*l* of a 1×10^{-3}M IF solution suffices with less than 50 μg of iron. The addition of more reagent decreased the absorbances.

Color Stability. The color of the zirconium system prepared at pH 3.65 was stable for 1 hr, while that of the iron system prepared at pH 4.0 was stable for 4 hr. Both color systems reached their maximum absorbances immediately after preparation.

Calibration Curves. From the foregoing results, the optimum conditions for determining zirconium and iron were derived. The procedures for preparing the calibration curves for these metal cations were as follows.

Zirconium(IV): To a sample solution containing up to 40 μg of zirconium in a 25-m*l* volumetric flask, we added 2.0 m*l* of a 1×10^{-3}M IF solution and 15 m*l* of a 2M acetate buffer solution with a pH of 3.65. After the solution had then been diluted to the mark with water, its absorbance was measured at 605 mμ against the reagent blank.

Iron(III): To a sample solution containing up to 50 μg of iron in a 25-m*l* volumetric flask, we added 1.8 m*l* of a 1×10^{-3}M IF solution and 10 m*l* of a 0.25M acetate buffer solution with a pH of 4.0. After the solution had then been diluted to the mark with water, its absorbance was measured at 590 mμ against the reagent blank.

The zirconium and iron systems obey Beer's law over the 2—40 and 1.5—50 μg ranges respectively in 25 m*l*. The optimum concentration ranges, as obtained from the curves drawn according to Ringbom,[5] are 10—30 μg for zirconium and 9—21 μg for iron. The molar absorptivities are 3.18×10^4 for zirconium and 1.81×10^4 for iron, while the sensitivities calculated[6] for $\log I_0/I=0.001$ are 0.0038 μg/cm^2 for zirconium and 0.0039 μg/cm^2 for iron. The reproducibilities of the methods, using 10 samples, each containing 20.94 μg of zirconium, and 9 samples, each containing 22.34 μg of iron, were then examined. The standard deviation were found to be 0.0028 absorbance unit, or 2.1%, for zirconium, and 0.0010, or 2.1%, for iron. The proposed method is comparable in sensitivity with the xylenol orange method[7] for zirconium and with the methylthymol blue method[8] for iron.

Considering the high sensitivity of zirconium(IV)-, iron(III)-, and others-IF complexes (Table 1), indoferron may well be considered a useful reagent for the spectrophotometric determination of these metal cations.

Effect of Diverse Ions. The effect of 29 cations and 12 anions on the zirconium(IV) and iron(III) determinations was examined separately. Many bi-, ter-, and quadrivalent metals and chelating agents interfered with both determinations, indicating that indoferron is not a selective reagent for zirconium and iron, in spite of its high sensitivity to these metals.

Composition of the Complexes. The compositions of the zirconium(IV) and the iron(III) complexes were determined by the method of con-

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[5] A. Ringbom, *Z. Anal. Chem.*, **115**, 332 (1938/9).

[6] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York (1950), p. 49.

[7] K. L. Cheng, *Talanta*, **2**, 61, 266 (1956).

[8] K. Tonosaki, This Bulletin, **39**, 425 (1966).

tinuous variation and by the mole-ratio method.

Zirconium(IV)-IF Complex. In the case of the former method, the maximum absorbance corresponded to a complex of the Zr(Ligand)$_3$ type at all the wavelengths investigated. The same results were also obtained by the mole-ratio method: the curves show sharp breaks at a zirconium(IV): ligand mole ratio of 1 : 3 (Fig. 5).

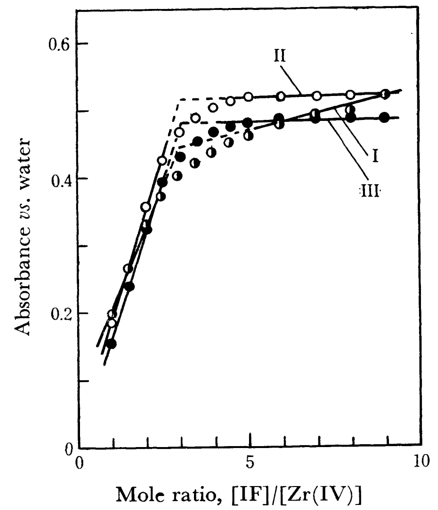

Fig. 5. Mole ratio method.
Zr(IV): 2.0×10^{-5}M, μ: 1.2, I: 565 mμ, II: 605 mμ III: 625 mμ, pH 3.65

Considering the ionic species of zirconium(IV) and the possibility of forming polymerized complexes, it is speculative to postulate a structure for the zirconium(IV)-IF complex. Therefore, no calculation of the formation constant was made.

Iron(III)-IF Complex. According to the method of continuous variation, the maximum absorbance corresponded to a complex of the Fe(Ligand)$_2$ type. Some of the results are shown in Fig. 6. The same results were also obtained by the mole-ratio method.

The apparent formation constant, K', was calculated from the curves shown in Fig. 6, using the relations:[9]

$$K' = C(1-\alpha)/(\alpha C)(2\alpha C)^2$$

$$\alpha = (E_m - E_s)/E_m$$

where C is the total concentration of the complex in moles per liter, α is the degree of dissociation, E_m is the maximum absorbance indicating that all the iron is present as a complex, and E_s is the absorbance at the stoichiometric molar ratio. The apparent formation constant at pH 4.0 was found to be 7.81×10^{10}.

Comparing the formation constants of the acetatocomplexes with those of hydroxocomplexes of iron(III),[10] it may be said that the latter complexes are not formed under the conditions investigated. Assuming that the indoferron serves as a terdentate ligand, the acetate ion in the acetatoiron(III) complexes may be eliminated by the chelate formation between iron(III) and indoferron. In other words, the coordination atoms of indoferron are found to be phenolic oxygen, nitrogen, and one of the two carboxyloxygens, and these atoms will coordinate with iron to form five- and six-membered rings.

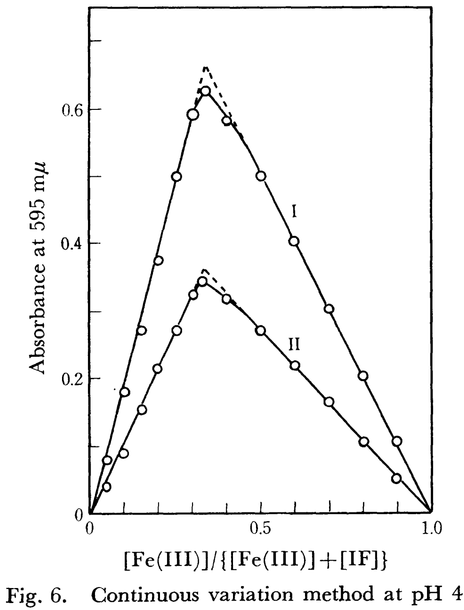

Fig. 6. Continuous variation method at pH 4.0.
[Fe(III)]+[IF]: I; 1.2×10^{-4}M, II; 0.6×10^{-4}M, μ: 0.5

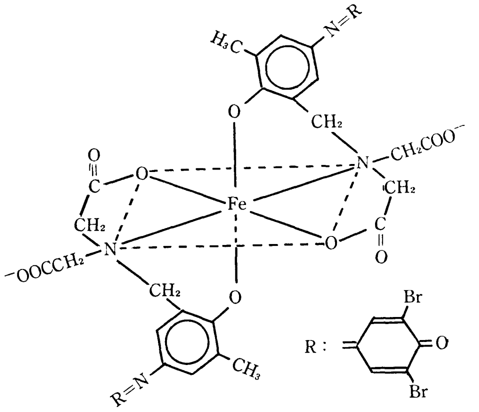

Fig. 7. Postulated structure for the complex Fe(III)(Ligand)$_2$.

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[9] A. E. Harvey, Jr., and D. L. Manning, *J. Amer. Chem. Soc.*, **72**, 4488 (1950).

[10] A. Ringbom, "Complexation in Analytical Chemistry," Interscience Publishers, New York (1963), pp. 298, 320: log $\beta_1=11.0$ ($\mu=3$) for hydroxoiron(III) complex, log $K_1=3.4$ ($\mu=0.1$) for acetatoiron(III) complex.

Thus, this structure for the complex may be postulated:

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