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The Spectrophotometric Determination of Scandium with Eriochrome Azurol G

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Some dyes of the triphenylmethane series react with many metallic ions in a weakly or a slightly acidic medium to form colored complexes. In preceding papers,[1,2] the present author and his co-workers described how pontachrome azure blue B and chromal blue G, dyes of this series, were excellent reagents for the spectrophotometric determination of scandium.

This paper will describe a spectrophotometric determination of scandium using eriochrome azurol G (sodium-2'',5'',6''-trichloro-4'-hydroxy-3,3'-dimethylfuchsone-5,5'-dicarboxylate, color index 43855), which is one of the compounds of this series. It is based on the reddish-violet complex formation between scandium ions and eriochrome azurol G in a slightly acidic medium. Several conditions under which small amounts of scandium can be determined, the influences of diverse ions, and the composition of the complex will be investigated. This reagent has been examined as an indicator of the titrimetric determination of potassium by tetraphenylborate and benzalkonium chloride.[3]

Experimental

Reagents and Apparatus. *Standard Scandium Solution.* 153 mg of scandium oxide (Mitsuwa Chemicals) were dissolved in small amounts of concentrated hydrochloric acid, and the solution was diluted to 1 *l* with water. This standard stock solution (100 ppm of scandium) was diluted further as required.

0.1% Eriochrome Azurol G Solution. Eriochrome azurol G (Tokyo Kasei Kogyo Co., Ltd., Tokyo) was further purified by recrystallization from ethanol before use, and then 0.1 g of it was dissolved in 100 m*l* of 95% ethanol. This reagent solution was stable for at least a month.

All the other reagents and apparatus used were the same as those reported previously.[2]

Procedure. Into a 25 m*l* volumetric flask place the standard solution or a sample solution containing 2.5—25 μg of scandium, and then add 2 m*l* of the 0.1% eriochrome azurol G solution. Add 10 m*l* of the buffer solution (pH 6.0, 0.2 M in acetate), mix thoroughly, and then dilute to the volume with distilled water. Measure the absorbance at 610 mμ using a reagent blank as a reference. Calculate the amount of scandium from the calibration curve.

Results and Discussion

Absorption Spectra. The absorption spectra of the reagent at various pH's are shown in Fig. 1. The maximum absorption of the reagent solution is found at 490 mμ below pH 4.5, at 430 mμ between pH 5.5 and 10, and at 590 mμ above pH 10.5. The absorbance curves of the scandium-eriochrome azurol G complex at various pH are shown in Fig. 2. The maximum absorption of the complex between 450 and 700 mμ is found at 610 mμ above pH 5.0. At pH 4.0, the complex in the visible region has two maxima, one at 600 mμ and another at 530 mμ. Below pH 3.5, however, the absorption maximum is found at 530 mμ.

Effect of the pH. The effect of the pH on the color reaction was investigated by taking absorbance measurements at 610 mμ of solutions containing scandium and eriochrome azurol G at various pH values. The results are shown in Fig. 3, from which it can be seen that the maximum absorbance of the scandium complex occurs in the pH range from 5.6 to 6.6. The reagent blank curve was

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[1] T. Shigematsu, K. Uesugi and M. Tabushi, *Bunseki Kagaku (Japan Analyst)*, **12**, 267 (1963).

[2] K. Uesugi, This Bulletin, **42**, 2051 (1969).

[3] T. Murakami, *Bunseki Kagaku (Japan Analyst)*, **14**, 880 (1965).

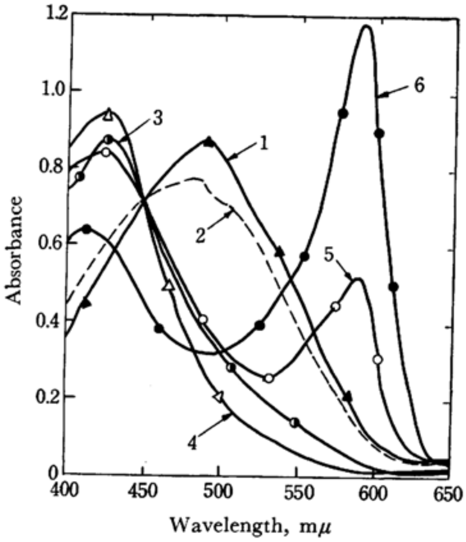

Fig. 1. Absorption spectra of reagent at various pH.
Reagent 80 ppm.
pH 1: 4.0, 2: 4.5, 3: 6.0, 4: 6.5—7.0, 5: 11.5, 6: 12.0

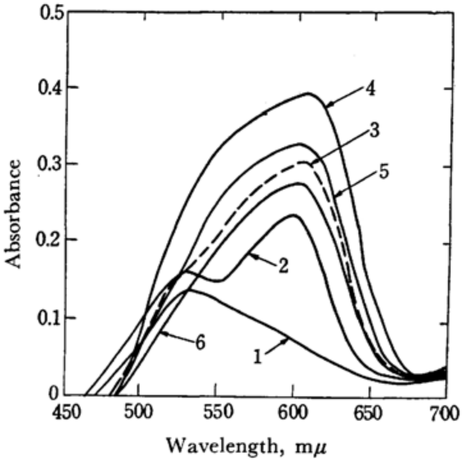

Fig. 2. Absorption spectra of scandium complex at various pH.
Reagent 80 ppm, Sc 0.6 ppm,
Reference: Reagent blank
pH 1: 3.4, 2: 4.0, 3: 5.0, 4: 6—6.4, 5: 7.0, 6: 8.0

obtained in the same manner, using the same amount of reagent. The acetate - acetic acid buffer, pH 6.0, was found to be satisfactory. The volume of the pH 6.0 buffer used was found to have no effect on the absorbance of a 0.5-ppm scandium solution over the range from 5 to 10 m*l* per 25 m*l* of solution.

Effect of Eriochrome Azurol G Concentration. The effect of the reagent concentration on the complex was investigated by measuring the absorbance at 610 mμ on solutions containing constant concentrations of scandium and the buffer and varying amounts of eriochrome azurol G. The absorbance increases as the reagent concentration increases. Therefore, it is desirable to keep the reagent concentration constant. Two milliliters of a 0.1% reagent solution was found to be sufficient for less than 1.0 ppm of scandium.

Color Stability. At room temperature, the formation of the scandium-eriochrome azurol G complex is substantially instantaneous, and its intensity is stable for at least one hour; only a 2% decrease in absorbance occurs after one hour when measured against a reagent blank.

Effect of the Temperature. The effect of the temperature on the color development was investigated by measuring the absorbance of solutions kept for 20 min at various temperatures. The absorbance does not change over the temperature range of 10 to 40°C. Over 40°C, the absorbance gradually decreases. Hence, normal temperature changes in the laboratory seem to have no effect.

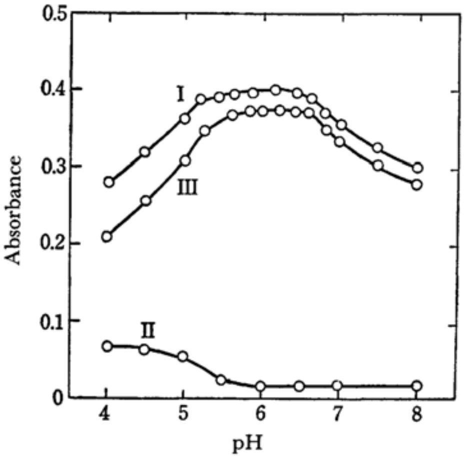

Fig. 3. Effect of pH on color intensity.
I: Reagent 80 ppm + Sc 0.6 ppm (Reference: water)
II: Reagent 80 ppm (Reference: water)
III: Reagent 80 ppm + Sc 0.6 ppm (Reference: Reagent blank)

Beer's Law and Sensitivity. Various amounts of a standard scandium solution containing up to 35 μg of scandium were used following the procedure mentioned above. Beer's law is obeyed over the range from 0.1 to 1.0 ppm of scandium. At 610 mμ the molar extinction coefficient is 29600. The spectrophotometric sensitivity is estimated to be 1.5×10^{-3} μg of scandium per cm^2, corresponding to $\log I_0/I = 0.001$.

The present method is very sensitive. Its sensitivity is much greater than that of the methods using eriochrome cyanine R (molar extinction coefficient, $\varepsilon=19000$),[4] pyrocatechol violet ($\varepsilon=17300$),[5] arsenazo I ($\varepsilon=17000$),[6] pontacyl violet 4BSN ($\varepsilon=13700$),[7] tiron ($\varepsilon=8000$),[8] and naphthyl azoxine S ($\varepsilon=8000$);[9] its sensitivity is slightly higher than that of chromazurol S ($\varepsilon=27000$),[10] and it is comparable with that of the method using pontachrome azure blue B ($\varepsilon=31500$),[1] chromal blue G ($\varepsilon=31400$),[2] and xylenol orange ($\varepsilon=29410$).[11]

TABLE 1. EFFECT OF DIVERSE IONS

Ion	added	as	Sc found (μg)
Ba(II)	100 μg	$BaCl_2$	9.9
Sr(II)	100 μg	$SrCl_2$	9.8
Mg(II)	100 μg	$MgCl_2$	10.1
Ca(II)	100 μg	$CaCl_2$	10.0
Mn(II)	100 μg	$MnSO_4$	10.0
Cu(II)	10 μg	$CuSO_4$	11.5
Zn(II)	100 μg	$ZnCl_2$	10.5
Cd(II)	100 μg	$CdCl_2$	9.9
Ni(II)	100 μg	$NiSO_4$	10.8
Co(II)	100 μg	$CoSO_4$	10.3
Pb(II)	100 μg	$Pb(NO_3)_2$	10.8
Hg(II)	100 μg	$HgCl_2$	9.8
Be(II)	5 μg	$BeCl_2$	28.9
Al(III)	5 μg	$Al(NO_3)_3$	22.3
Fe(III)	10 μg	$FeCl_3$	20.4
Cr(III)	100 μg	Cr-alum	8.0
Mo(VI)	100 μg	Na_2MoO_4	10.0
UO_2(II)	10 μg	$UO_2(NO_3)_2$	10.3
Y(III)	10 μg	YCl_3	12.1
La(III)	10 μg	$LaCl_3$	11.0
Ce(III)	10 μg	$CeCl_3$	11.2
Nd(III)	10 μg	$NdCl_3$	11.5
Gd(III)	10 μg	$GdCl_3$	11.1
Dy(III)	10 μg	$DyCl_3$	11.5
Er(III)	10 μg	$ErCl_3$	11.7
Th(IV)	10 μg	$Th(NO_3)_4$	11.0
Sulfate	100 mg	Na_2SO_4	10.5
Chloride	100 mg	NaCl	10.1
Nitrate	100 mg	KNO_3	10.2

Sc : 10.0 μg/25 m*l*

Precision and Accuracy. Nine determinations of 0.5 ppm of scandium gave a standard deviation of ±0.0074 ppm or a relative standard deviation of ±1.5%.

Effect of Diverse Ions. The effect of 26 cations and some anions on the determination of scandium was examined (Table 1). Many diverse cations, especially beryllium, copper(II), aluminum, iron(III), yttrium, thorium, and rare earth elements, interfere seriously with the determination of scandium, for they form complexes with eriochrome azurol G under the present experimental conditions (Fig. 4). The following anions do not interfere under the conditions described: sulfate, chloride, nitrate, and acetate, even when they are present in an anion-to-scandium ratio of 1 to 6000. The presence of oxalate, fluoride, citrate, and EDTA bleaches the color of the complex.

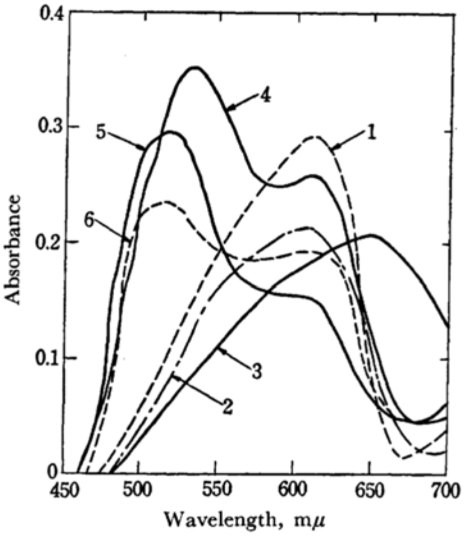

Fig. 4. Absorption spectra of beryllium, aluminum, iron(III), yttrium, lanthanum, and neodymium complexes at pH 6.0.
Reagent 80 ppm, Reference: Reagent blank
1: Be 0.15 ppm, 2: Al 0.13 ppm, 3: Fe(III) 0.3 ppm, 4: Y 2 ppm, 5: La 2 ppm, 6: Nd 2ppm

The absorption curves of the complexes of beryllium, aluminum, iron(III), yttrium, and some rare earth elements at pH 6.0 are shown in Fig. 4. The maximum absorbances of the beryllium and aluminum complexes are at 610 mμ, much like that of the scandium complex, and that of iron(III) complex is shifted toward a longer wavelength. The complexes of yttrium, lanthanum, gadolinium, and erbium have two absorption maxima, as is shown in Fig. 4.

Complex Formation. The composition of the scandium-eriochrome azurol G complex was

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[4] T. Fujinaga, T. Kuwamoto, S. Tsurubo and K. Kuwabara, *Bunseki Kagaku* (*Japan Analyst*), **13**, 127 (1964).

[5] S. P. Onosova and G. K. Kuntsevich, *Zh. Anal. Khim.*, **20**, 802 (1965).

[6] H. Onishi and C. V. Banks, *Anal. Chim. Acta*, **29**, 240 (1963).

[7] T. Shigematsu and K. Uesugi, *Bunseki Kagaku* (*Japan Analyst*), **16**, 467 (1967).

[8] H. Hamaguchi, N. Onuma, R. Kuroda and S. Sugisita, *Talanta*, **9**, 563 (1962).

[9] T. Shimizu, *Bunseki Kagaku* (*Japan Analyst*), **16**, 233 (1967).

[10] R. Ishida and N. Hasegawa, This Bulletin, **40**, 1153 (1967).

[11] O. V. Kon'kova, *Zh. Anal. Khim.*, **19**, 73 (1964).

determined by the continuous-variation method[12] and the mole-ratio method.[13] The results indicated that a 1 : 2 complex between scandium and eriochrome azurol G is formed at pH 6.0, and a 1 : 1 complex below pH 4.0. The formation constant of the scandium complex was determined spectrophotometrically by the same method as in a previous paper.[2] The formation constant for the complex at pH 6.0 and 25°C was calculated, from the curves of the continuous variation, as 2.6×10^{10}.

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[12] P. Job, *Ann. Chem.* **9**, 113 (1928).

[13] J. H. Yoe and A. I. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).