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The Spectrophotometric Determination of Scandium with Chromal Blue G

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For the spectrophotometric determination of scandium, various workers have proposed many organic reagents including alizarin red S,[1,2] oxine,[3] tiron,[4] morin,[5] naphthyl azoxine S,[6] arsenazo,[7] sulfonazo,[8] pontachrome azure blue B,[9] eriochrome cyanine R,[10] xylenol orange,[11] pontacyl violet 4BSN,[12] and chromazurol S.[13]

In this paper, a new method for the spectrophotometric determination of scandium using chromal blue G (sodium-2″-chloro-4″-nitro-4′-hydroxy-3,3′-dimethylfuchsone-5,5′-dicarboxylate, color index 43835), similar in structure to pontachrome azure blue B, eriochrome cyanine R, and chromazurol S, will be described. The method is based on the highly-sensitive colored reaction of chromal blue G with scandium in an acetate

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buffer solution. It will be found that chromal blue G is a more sensitive reagent for scandium than eriochrome cyanine R10) or chromazurol S,13) and that the proposed method is comparable in sensitivity to the method using pontachrome azure blue B.9)

Experimental

Reagents. *Standard Scandium Solution.* The standard solution of scandium was prepared by dissolving 153 mg of scandium oxide (Mitsuwa Chemicals) in 50 m*l* of concentrated hydrochloric acid and then by diluting the solution to 1 *l*. This solution contained 100 μg of scandium per m*l*. This stock solution was then diluted to the concentration required for each experiment.

Chromal Blue G Solution. The chromal blue G (Geigy Company, Inc., New York, U.S.A.) was purified by recrystallization from ethanol before use, and 0.1 g of it was dissolved in 100 m*l* of 95% ethanol. This solution was stable for at least a month.

Buffer Solution (*pH* 6.0). A buffer solution of pH 6.0 was prepared by mixing a 0.2 M acetic acid solution and a 0.2 M sodium acetate solution.

All other reagents were analytical grade in quality and were used without further purification.

Apparatus. Absorbance measurements were made with a Hitachi spectrophotometer, model 139, using 1.00-cm matched quartz cells. The pH measurements were carried out with a Hitachi-Horiba glass electrode pH meter, model M-4.

The Standard Procedure for the Determination of Scandium. Transfer the sample solution containing 3—30 μg of scandium to a 25 m*l* volumetric flask and add 2 m*l* of the 0.1% chromal blue G solution. Then add 10 m*l* of the buffer solution (pH 6.0), shake well, and make up to the mark with distilled water. After 20 min, measure the absorbance at 590 mμ, using a reagent blank solution treated in a similar manner as a reference.

Results and Discussion

Absorption Curves. The absorption curves of the reagent solution at various pH values are shown in Fig. 1. The maximum absorption of the reagent solution are found at 480 mμ below pH 4.0, at 430 mμ over the pH range from 5.5 to 10.0, and at 590 mμ above pH 10.5. The absorption curves of the scandium complex at different pH are shown in Fig. 2. The curves in Fig. 2 were obtained by measuring the absorbance of colored solutions containing 0.6 ppm of scandium against a reagent blank containing the same amount of the reagent. The maximum absorption of the complex is found at 590 mμ in acidic media, above pH 7.0, the position of the maximum absorption shifts toward a longer wavelength.

Effect of the pH on Color Development. The effect of the pH on the color development of the scandium complex was examined by measuring the absorbance of a colored solution at 590 mμ. The results are shown in Fig. 3, from which it can be seen that the maximum intensity can be obtained in the pH range from 5.8 to 6.5. An acetic acid-acetate buffer solution, pH 6.0, was found to be satisfactory for this purpose.

Rate of the Color Development. The color of the scandium complex gradually develops at room temperature; the full color is obtained 15 minutes after preparation and then remains almost constant for at least an hour.

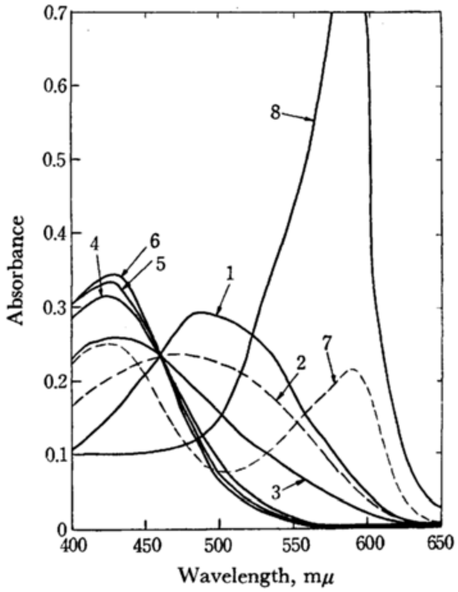

Fig. 1. Absorption spectra of reagent at various pH.
Reagent 20 ppm
pH 1: 4.0, 2: 4.5, 3: 5.0, 4: 5.5, 5: 6.0—6.5, 6: 7.5, 7: 11.5, 8: 12.5

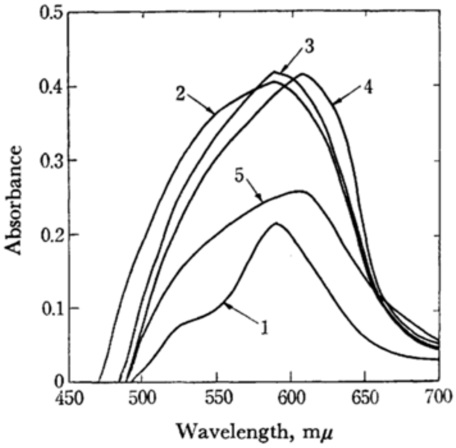

Fig. 2. Absorption spectra of scandium complex at various pH.
Sc 0.6 ppm, Reagent 80 ppm
Reference: Reagent blank
pH 1: 4.0, 2: 5.5, 3: 6.0—6.5, 4 :7.0, 5: 8.0

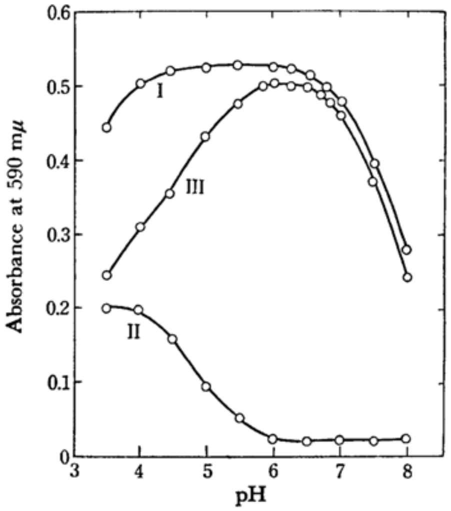

Fig. 3. Effect of pH on color intensity.
I: Reagent 80 ppm+Sc 0.72 ppm (Reference: water)
II: Reagent 80 ppm (Reference : water)
III: Reagent 80 ppm+Sc 0.72 ppm (Reference: Reagent blank)

Effect of Amount of the Reagent on Color Intensity. The effect of variable amounts of the reagent on the color development was examined for a definite concentration of scandium. The absorbance of the scandium complex at 590 mμ gradually increases at higher reagent concentrations. Therefore, it is necessary to keep constant the amount of the reagent added. Two milliliters of a 0.1% solution of the reagent were found to be sufficient for less than 1.2 ppm of scandium.

Effect of Temperature on the Color Development. There was no variation in the absorbance of the color system over the temperature range from 10 to 30°C.

Beer's Law. The scandium complex is found, using the standard procedure, to follow Beer's law up to 1.2 ppm of scandium. The molar extinction coefficient is 3.14×10^4 at 590 mμ. The spectrophotometric sensitivity of the reaction is 1.4×10^{-3} μg Sc/cm^2, corresponding to $\log I_0/I = 0.001$.

Effect of Diverse Ions. The effect of 28 cations and some anions on the determination of scandium were examined. Copper(II), cobalt(II), beryllium, iron(III), chromium(III), yttrium, and rare earth elements interfere. These cations give a positive error in the determination of scandium, as these also form colored complexes with the reagent in a slightly acidic medium. Chloride, nitrate, sulfate, and acetate do not interfere, even at a high concentration.

Complex Formation. The method of continuous variations was applied for the determination of the component of the proposed scandium complex with chromal blue G. The results are shown in Fig. 4, which indicates that a 1-to-2 complex is formed between scandium and chromal blue G. These results were confirmed by the mole-ratio method.

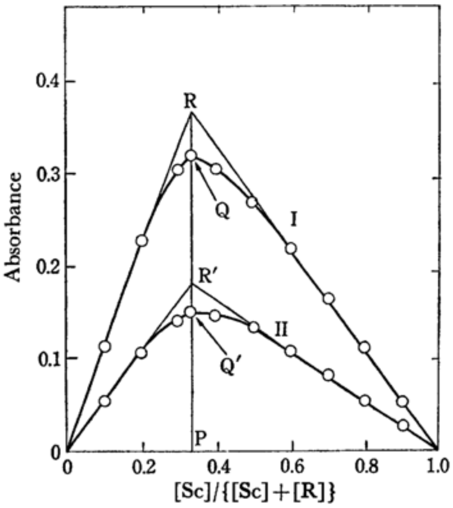

Fig. 4. Continuous variation method.
pH 6.0, 25°C
I: $[\mathrm{Sc}]+[\mathrm{R}]=7.0\times10^{-5}$ M
II: $[\mathrm{Sc}]+[\mathrm{R}]=3.5\times10^{-5}$ M

The formation constant was calculated from the curves obtained by the continuous-variation method. As the mole ratio of the scandium-chromal blue G complex is 1 : 2, the reaction can be expressed as:

$$\begin{array}{llll} \mathrm{Sc} + 2\mathrm{R} & \rightleftharpoons & \mathrm{ScR_2} & \\ 0 \quad 0 & & C & \text{initial concentration} \\ \alpha C \quad 2\alpha C & & C(1-\alpha) & \text{equilibrium concentration} \end{array}$$

where C is the total concentration of the complex in moles per liter assuming no dissociation and where α is the degree of dissociation. The formation constant, K, was estimated from the curves shown in Fig. 4 on the basis of the following relationships:[14]

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

where E_m is the maximum extinction of the complex when all the scandium is present in the form of the complex, and where E_s is the actual absorbance of the complex. The value of E_m and E_s correspond to PR or PR′ and PQ or PQ′ respectively. The formation constant at pH 6.0 and 25°C was estimated to be 2.8×10^{10}.

The proposed method using chromal blue G has several advantages as a reagent for scandium: the maximum absorbance can be obtained rapidly; no extraction of the complex is required, since the scandium complex is water-soluble; it is also comparable with the method using pontachrome

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azure blue B,[9] and this method is much more sensitive than any other of the methods mentioned above.

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