Spectrophotometric Determination of Scandium with Semimethylxylenol Blue

Spectrophotometric Determination of Scandium with Semimethylxylenol Blue

Joichi UEDA, Yukiko KONISHI and Sigehiro KAGAYA

Department of Chemistry, Faculty of Education,
Kanazawa University,
Kakumamachi, Kanazawa, 920-11, Japan

Summary-A reagent of the sulfophthalein nitrilodiacetate type, Semimethylxylenol Blue (SMXB), was synthesized, purified, and applied to the spectrophotometric determination of scandium. Scandium produced a water-soluble red-violet complex with SMXB. The absorption maximum of the colored solution occurred at 557-560 nm, and the absorbance was constant over the pH range from 2.5 to 2.9. The relation between the absorbance of the complex and the concentration of scandium was linear over the range of 0.2−1.6 μg Sc/ml. The molar extinction coefficient of the complex and the sensitivity of the determination were 3.0×10^4 and 0.0015 μg Sc/cm^2 for $\log(I_0/I)=0.001$, respectively. From these data, the following procedure is presented for the determination of scandium.

A sample solution containing 5-40 μg of scandium is taken into a 25 ml of volumetric flask and pH is adjusted to 2.7 by the addition of the buffer solution. Then 3 ml of 0.05% SMXB solution is added. After making up the volume to 25 ml, an absorbance is measured at 559 nm against a reagent blank.

The chemical formula was found to be Sc(SMXB) by the mole ratio and the continuous variation methods.

INTRODUCTION

As a part of the investigation for the spectrophotometric determination of metal ions with sulfophthalein derivatives, the authors synthesized Semimethylxylenol Blue, 3-[N, N−di(carboxymethyl)aminomethyl]-p-xylenolsulfophthalein, from Paraxylenol Blue and iminodiacetic acid by the Mannich condensation,[1] examined its color reactions with metal ions, and proposed the spectrophotometric methods for the determination of thorium,[2] iron(III),[3] aluminum,[3] zirconium,[4] gallium,[5] palladium,[6] bismuth(III),[6] hafnium,[7] magnesium,[8] and calcium.[8] Semimethylxylenol Blue (SMXB) also reacted with scandium in acidic medium to form a water-soluble red-violet complex. So, the possibility of using this reagent for the spectrophotometric determination of scandium was examined, and it was recognized that SMXB was a suitable reagent for this element as regards both the sensitivity and the selectivity

Received on Sept. 16th, 1994.

and could be applied to the determination over the concentration range from 0.2 to 1.6 μg/ml of scandium. The proposed method here is nearly as specific as the methods using such reagents with similar structure to SMXB as Xylenol Orange, [9),10)] Methylthymol Blue,[11)] and Methylxylenol Blue[12)] and has higher sensitivity than those methods.

This paper describes the fundamental conditions for the spectrophotometric determination of scandium utilizing SMXB as the photometric reagent.

EXPERIMENTAL

Reagents and Apparatus

A solution containing about 1mg/ml of scandium was prepared by dissolving guaranteed reagent grade scandium chloride in a small amount of hydrochloric acid and diluting with distilled water. The concentration of scandium was determined by the complexometric titration using Xylenol Orange as an indicator. This solution was diluted with distilled water as required. A 0.05% SMXB solution was prepared by dissolving a weighed amount of SMXB in distilled water. The SMXB was synthesized from Paraxylenol Blue, iminodiacetic acid, and formaldehyde by the Mannich condensation, separated from the reaction mixture on a cellulose column by 1-butanol saturated with 0.1% acetic acid, and then obtained in the free acid form

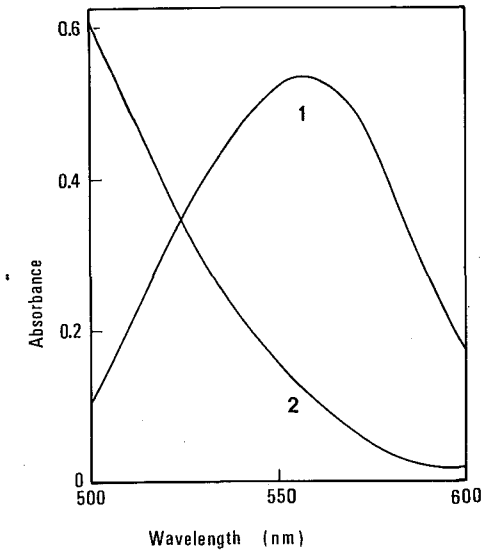

Fig. 1. Absorption curves of scandium-SMXB complex in a 25 ml aqueous solution containing 20 μg of scandium and 3 ml of 0.05% SMXB solution at pH 2.7 (1) and of the reagent blank (2). The absorbances were measured against the reagent blank (1) and water (2) as references.

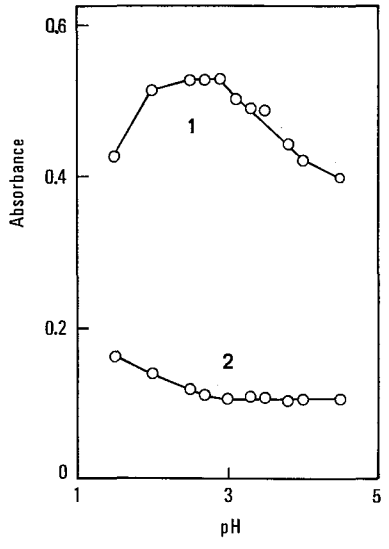

Fig. 2. Effect of pH on the absorbance of scandium-SMXB complex (1) and the reagent blank (2), examined with a 25 ml aqueous solution containing 20 μg of scandium and 3 ml of 0.05% of SMXB solution. The absorbances were measured at 559 nm against the reagent blank (1) and water (2) as references.

by passing the fraction of SMXB through a column of cation-exchange resins.[2,3] For the pH adjustment, 0.1 mol/l hydrochloric acid-0.1 mol/l sodium chloride-0.1 mol/l glycine buffer solution was used. All the other regents used were of guaranteed reagent grade.

A Hitachi-Perkin-Elmer model 139 spectrophotometer with 1 cm glass cells and a Hitachi-Horiba model M-5 glass electrode pH meter were used for the absorbance and the pH measurements, respectively.

Recommended procedure

A sample solution containing 5-40 μg of scandium is taken into a 25 ml of volumetric flask and pH is adjusted to 2.7 by the addition of 10 ml of 0.1mol/l hydrochloric acid-0.1 mol/l sodium chloride-0.1 mol/l glycine buffer solution. Then 3 ml of 0.05% SMXB solution is added. After making up the volume to 25 ml, an absorbance is measured at 559 nm against a reagent blank as a reference.

RESULTS AND DISCUSSION

Absorption curves

The absorption curve of the scandium complex obtained by the recommended procedure is shown in Fig. 1. The colored solution of the scandium complex has an absorption maximum at 557-560 nm and the peak of the spectrum does not shift with the change of the pH of the solution over the range from pH 2.5 to 2.9. In this Figure, the absorption spectrum of the reagent blank is also shown.

Optimum conditions for color development

The effect of pH on the color development of the solution containing 20 μg of scandium was examined, measuring the absorbance of colored mixture at 559 nm. As the result is shown in Fig. 2, the range in which the maximum and nearly constant absorbance was obtained was pH 2.5-2.9. So, the pH of the solution was adjusted at 2.7 for the color development. As the buffer solution for the pH adjustment, 0.1 mol/l hydrochloric acid-0.1mol/l sodium chloride- 0. 1 mol/l glycine solution was chosen in this experiment. The addition from 5 to 15 ml of this buffer solution had no effect on the color intensity of the scandium complex. The amount of 0.05% SMXB solution was varied to study the effect of the reagent concentration on the absorbance. The maximum color formation was obtained by adding from 2 to 5 ml of the reagent solution for 20 μg of scandium (Fig. 3). The color reaction with scandium and SMXB was rapid at a room temperature and the full color development occurred within a few minutes after SMXB was added. The color, once developed, was very stable and the absorbance remained almost constant for at least 75 min (Fig. 4). The calibration curve for scandium prepared according to the recommended procedure is shown in Fig. 5. A straight line passing through the origin was obtained over the concentration range from 0.2 to 1.6 μg/ml of scandium. The molar extinction coefficient of the complex and the sensitivity of the determi-

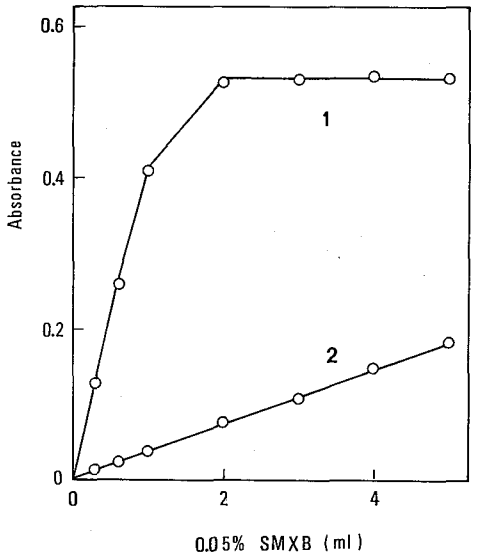

Fig. 3. Effect of SMXB concentration on the absorbance of scandium-SMXB complex (1) and the reagent blank (2), examined with a 25 ml aqueous solution containing 20 μg of scandium at pH 2.7. The absorbances were measured at 559 nm against the reagent blank (1) and water (2) as references.

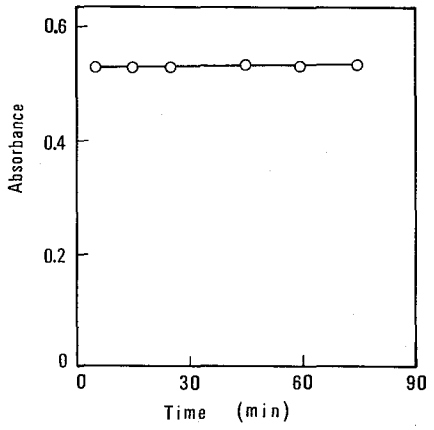

Fig. 4. Effect of standing time on the absorbance of scandium-SMXB complex examined with a 25 ml aqueous solution containing 20 μg of scandium and 3 ml of 0.05% SMXB solution at pH 2.7. The absorbance was measured at 559 nm against a reagent blank as a reference.

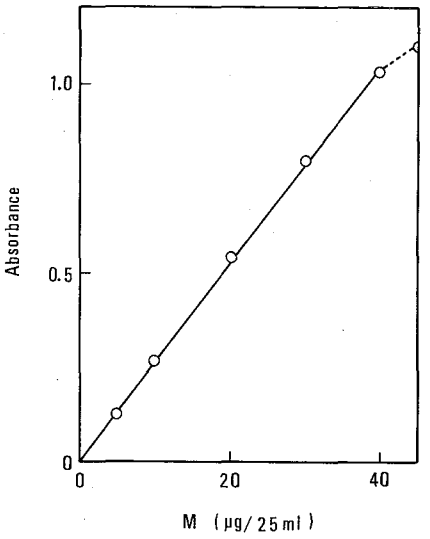

Fig. 5. Calibration curve of scandium in a 25 ml aqueous solution containing 3 ml of 0.05% SMXB solution at pH 2.7. The absorbance was measured at 559 nm against a reagent blank as a reference.

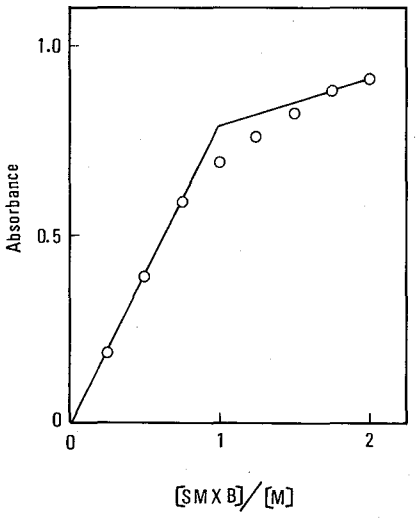

Fig. 6. The mole ratio method examined with a 25 ml aqueous solution containing a constant amount of scandium, 7.1×10^{-7} M, and various amounts of SMXB at pH 2.7. The absorbance was measured at 559 nm against a reagent blank as a reference.

nation according to Sandell's expression which were calculated from the curve were 3.0×10^4 and 0.0015 μg Sc/cm^2, respectively. The reproducibility of the method, expressed by the relative standard deviation of the absorbances which were obtained from ten repeat determinations, was 2.0%.

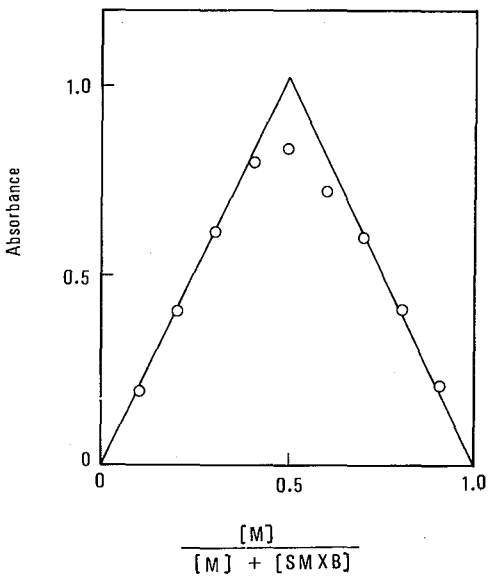

Fig. 7. The continuous variation method examined with a 25 ml aqueous solution at pH 2.7 in which the total mole of scandium and SMXB was held at 1.8×10^{-6} M. The absorbance was measured at 559 nm against a reagent blank as a reference.

The effect of diverse ions

According to the recommended procedure, the effect of twenty diverse ions on the determination of 20 μg of scandium was examined. Concerning anions, the presence of 10 mg each of acetate and tartrate did not interfere with the determination, but fluoride and citrate did seriously. For cations, scandium could be determined within 5% error in the presence of 500 μg each of beryllium, magnesium, calcium, zinc, mercury(II), yttrium, and lanthanum, 100 μg each of cobalt and nickel, and 50 μg each of aluminum, tin(IV), and lead. Indium, bismuth(III), copper, and iron(III) interfered with the determination, but the effect of iron(III) could be eliminated by the addition of 3 ml of 4% L-ascorbic acid.

The composition of the complex

The composition of the scandium-SMXB complex was examined at pH 2.7 by the mole ratio and the continuous variation methods, measuring the absorbance at the wavelength of 559 nm. In the former method, various amounts of SMXB were added to a constant amount of scandium, 7.1×10^{-7} M in 25ml, and in the latter method, the total mole of scandium and SMXB was held constant at 1.8×10^{-6} M in 25 ml. As the results were shown in Figs. 6 and 7, both the equivalence point in the mole ratio method and the maximum point of the absorbance in the continuous variation method indicated that the mole ratio between scandium and SMXB was 1 : 1.

CONCLUSIONS

SMXB is recommended as a spectrophotometric reagent for scandium, owing to its excellent complex formation ability. The method proposed here has a high sensitivity and a good precision. The optimum concentration range for the determination is 0.2-1.6 μg/ml of scandium. The molar absorptivity of the complex was 3.0×10^4 and the reproducibility of this

method, expressed by the relative standard deviation of the absorbances which were obtained from ten repeat determinations, was 2.0%.

REFERENCES

1. M. Otomo, *Bunseki kagaku*, **21**, 442 (1972).
2. J. Ueda, *Nippon Kagaku Kaishi*, **1977**, 350 (1977).
3. J. Ueda, *Bull. Chem. Soc. Jpn.*, **51**, 773 (1978).
4. J. Ueda, *Nippon Kagaku Kaishi*, **1979**, 1115 (1979).
5. J. Ueda and T. Kitadani, *Nippon Kagaku Kaishi*, **1982**, 1914 (1982).
6. J. Ueda and K. Kadowaki, *Bull. Chem. Soc. Jpn.*, **56**, 1968 (1983).
7. J. Ueda, S. Kosumi and S. Kagaya, *Bull. Fac. Educ. Kanazawa Univ.*, **41**, 71 (1992).
8. J. Ueda, K. Ohta and S. Kagaya, *Bull. Fac. Educ. Kanazawa Univ.*, **43**, 53 (1994).
9. O. V. Kon'kova, *Zhur. Anal. Khim.*, **19**, 73 (1964) ; *Anal. Abstr.*, **12**, 1663 (1965).
10. S. S. Berman, G. R. Duval and D. S. Russell, *Anal. Chem.*, **35**, 1392 (1963).
11. M. K. Akhmedli and D. G. Gambarov, *Zh. Analit. Khim.*, **22**, 1183 (1967) ; *Anal. Abstr.*, **16**, 2391 (1969).
12. J. Ueda, *Nippon Kagaku Kaishi*, **1973**, 1467 (1973).