Spectrophotometric Determination of Iron(III) and Aluminium with Semimethylxylenol Blue

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Semimethylxylenol Blue (SMXB) reacts with iron(III) and aluminium to form water-soluble colored complexes. The colored solution of the iron(III) complex shows a maximum absorption at 580—581 nm, while that of the aluminium complex shows it at 554—555 nm. The absorbances of the solutions are constant over the pH range from 1.2 to 1.5 and from 2.5 to 2.9, respectively. Beer's law is obeyed up to 1.4 μg cm^{-3} of iron(III) and 1.0 μg cm^{-3} of aluminium. Their molar extinction coefficients are 3.38×10^4 and 2.91×10^4, respectively. As a result of the investigation of the composition of the iron(III) or aluminium complex, the mole ratio of metal and SMXB was estimated to be 1 : 1. Among the 45 diverse ions examined, gallium, tin(IV), bismuth(III), zirconium, and vanadium(V) interfered with iron(III) determination, and gallium, indium, bismuth(III), scandium, titanium(IV), zirconium, vanadium(V), iron(III), fluoride, and oxalate interfered with aluminium determination. Consecutive determination of iron(III) and aluminium was also studied.

Semimethylxylenol Blue (SMXB) is obtained as one of the products in the synthesis of Methylxylenol Blue by the Mannich condensation of Paraxylenol Blue, formaldehyde, and iminodiacetic acid. It is a monosubstituted derivative of Paraxylenol Blue, while Methylxylenol Blue is a disubstituted derivative.[1] In the preceding paper,[2] the author proposed a method for the determination of thorium, based on the sensitive color reaction of SMXB with thorium. This reagent also reacts with iron(III) and aluminium to form water-soluble colored complexes. So the possibility of using this reagent for the spectrophotometric determinations of these elements was examined, and it was found that SMXB was a suitable reagent for these elements, especially for iron(III), as regards both sensitivity and selectivity, and could be applied to the determinations of up to 1.4 μg cm^{-3} of iron(III) and up to 1.0 μg cm^{-3} of aluminium. In the present methods, iron(III) interferes with the determination of aluminium, giving a positive error, but it can be determined without interference from aluminium. Utilizing these facts, the consecutive determination of iron(III) and aluminium was also studied, and satisfactory results were obtained with the solutions containing 0.16—2.0 μg cm^{-3} of iron(III) and 0.16—1.2 μg cm^{-3} of aluminium.

The present methods for both iron(III) and aluminium are nearly as specific as the methods using such reagents with similar structures to SMXB as Xylenol Orange,[3,4] Methylthymol Blue,[5,6] and Methylxylenol Blue,[7,8] and have higher sensitivities than these methods. Further, this reagent is more sensitive than the most common reagents for iron, such as 1,10-phenanthroline,[9] 4,7-dihydroxy-1,10-phenanthroline,[10] 2,2′-bipyridine,[9] and 2,4,6-tri-2-pyridyl-1,3,5-triazine,[11] and more sensitive than those for aluminium such as Aluminon,[12] Alizarin S,[12] Eriochrome Cyanine R,[13] Stilbazo,[14] and Chromazurol S.[15]

Experimental

Reagents. *Standard Iron(III) Solution*: A solution containing about 1 mg cm^{-3} of iron(III) was prepared by dissolving guaranteed reagent grade iron(III) nitrate in a small amount of nitric acid and diluting with distilled water. The solution was standardized by the complexometric back-titration with a standard solution of thorium using Xylenol Orange as an indicator. This solution was diluted as required.

Standard Aluminium Solution: A solution containing about 1 mg cm^{-3} of aluminium was prepared by dissolving guaranteed reagent grade aluminium nitrate in a small amount of hydrochloric acid and diluting with distilled water. The solution was standardized by the complexometric back-titration with a standard solution of zinc using Xylenol Orange as an indicator. This solution was diluted as required.

SMXB Solution: A 0.05% SMXB solution was prepared by dissolving a weighed amount of the reagent in distilled water. The SMXB was prepared by the method described in the preceding paper[2] : it 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 by passing the fraction of SMXB through a column of cation-exchange resins.

Buffer Solutions: The pH was adjusted with 1 mol dm^{-3} sodium acetate-1 mol dm^{-3} hydrochloric acid for the determination of iron(III) and 0.1 mol dm^{-3} glycine-0.1 mol dm^{-3} sodium chloride-0.1 mol dm^{-3} hydrochloric acid for that of aluminium.

All the other reagents used were of guaranteed reagent grade.

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

Recommended Procedures. *Determination of Iron(III)*: A sample solution containing up to 35 μg of iron(III) is transferred to a 25 cm^3 volumetric flask. Then 10 cm^3 of the buffer solution of sodium acetate-hydrochloric acid and 3 cm^3 of 0.05% SMXB solution are added. After making up the volume to 25 cm^3 (the final pH: 1.3) and allowing it to stand for 20 min, the absorbance is measured at 580 nm against the reagent blank.

Determination of Aluminium: A sample solution containing up to 25 μg of aluminium is taken into a 50 cm^3 Erlenmeyer's flask. Then, 5 cm^3 of the buffer solution of glycine-sodium chloride-hydrochloric acid, 2 cm^3 of 0.05% SMXB, and 10 cm^3 of dioxane are added. After being kept for a few minutes in a boiling water bath, the solution is cooled with running water, transferred to a 25 cm^3 volumetric flask, and diluted to the mark with water (the final pH : 2.6). The absorbance is measured at 555 nm within 1 h against the reagent blank.

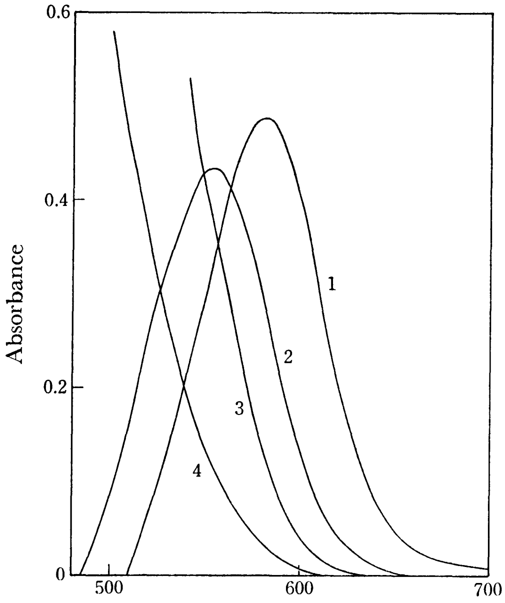

Fig. 1. Absorption curves of iron(III) and aluminium complexes.

1: Fe(III) 20 μg/25 cm^3, 0.05% SMXB 3 cm^3, pH 1.3, reference: reagent blank.

2: Al 10 μg/25 cm^3, 0.05% SMXB 2 cm^3, dioxane 10 cm^3, pH 2.6, reference: reagent blank.

3, 4: Reagent blanks of 1 and 2 respectively, reference: water.

Results and Discussion

Absorption Curves. The absorption curves of iron(III) and aluminium complexes obtained by the recommended procedures are shown in Fig. 1.

The colored solution of the iron(III) complex had an absorption maximum at 580—581 nm, while that of the aluminium complex had it at 554—555 nm.

The Effect of pH. As shown in Fig. 2, the ranges in which the maximum and nearly constant absorbance was obtained were found to be pH 1.2—1.5 for iron(III) and pH 2.5—2.9 for aluminium.

The Stability of the Color. Iron(III) Complex: The full color development was obtained about 10 min after the reagent was added. The color, once developed, was very stable, and the absorbance remained constant for at least several hours.

Aluminium Complex: The color reaction of SMXB with aluminium was very slow at a room temperature. But the reaction time could be considerably shortened by heating the solution in a boiling water bath, and the maximum color development was obtained within only a few minutes. So heating for 3 min in a hot water bath was adopted in further experiments. On the other hand, the absorbance of the resultant colored solution decreased gradually with the time of standing. However, it was found that by adding 7 to 13 cm^3 of dioxane the absorbance remained almost constant for at least 1 h after the color development and was higher by about 14% than the absorbance of the colored solution in the absence of dioxane. Accordingly, 10 cm^3 of dioxane was always used in these experiments.

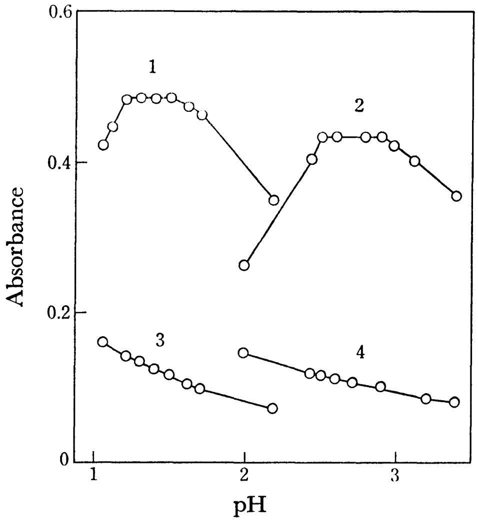

Fig. 2. Effect of pH.

1: Fe(III) 20 μg/25 cm^2, 0.05% SMXB 3 cm^3, wavelength 580 nm, reference: reagent blank.

2: Al 10 μg/25 cm^3, 0.05% SMXB 2 cm^3, dioxane 10 cm^3, wavelength 555 nm, reference: reagent blank.

3, 4: Reagent blanks of 1 and 2 respectively, reference: water.

The Effect of the Amount of SMXB. The maximum and almost constant absorpances were obtained by adding from 2.7 to 6 cm^3 of 0.05% SMXB solution for 20 μg of iron(III) and from 1.5 to 6 cm^3 for 10 μg of aluminium.

The Effect of the Amount of the Buffer Solution. The addition of from 3 to 15 cm^3 of 1 mol dm^{-3} sodium acetate–1 mol dm^{-3} hydrochloric acid buffer solution had no effect on the color intensity of the iron(III) complex. In the case of aluminium, there was no change in the absorbance when 3 to 10 cm^3 of 0.1 mol dm^{-3} glycine–0.1 mol dm^{-3} sodium chloride–0.1 mol dm^{-3} hydrochloric acid buffer solution was used. In this case, the use of the acetate buffer instead of the glycine–sodium chloride–hydrochloric acid buffer was unsatisfactory, because the decrease of the absorbance was induced immediately after the color development, even if dioxane was present.

Calibration Curves. Under the conditions described in the recommended procedures, Beer's law was obeyed up to 1.4 μg cm^{-3} of iron(III) and up to 1.0 μg cm^{-3} of aluminium. The molar absorptivities calculated from the curves were found to be 3.38×10^4 for iron(III) and 2.91×10^4 for aluminium, while the sensitivities for $\log I_0/I = 0.001$ were 0.0016 μg Fe(III)/cm^2 and 0.0009 μg Al/cm^2. The reproducibilities of the methods, expressed by the relative standard deviations of the absorbances which were obtained from five repeat determinations, were 0.47% for iron(III) and 0.87% for aluminium.

The Effect of Diverse Ions. The effect of 45 diverse ions on the determination of 20 μg of iron(III) or 10 μg of aluminium was examined. The results obtained are summarized in Table 1.

For the iron(III) determination, 24 cations such as alkali metals, alkaline earth metals, lead, copper, zinc,

TABLE 1. EFFECTS OF DIVERSE IONS

Ion	A: Amount added (mg)	A: Fe(III) found (μg)	B: Amount added (μg)	B: Al found (μg)	Ion	A: Amount added (mg)	A: Fe(III) found (μg)	B: Amount added (μg)	B: Al found (μg)
Li^+	1	20.0	500	9.9	Ce^{3+}	1	19.9	500	10.5
K^+	1	20.3	500	9.9	Ti^{4+}	0.1	20.2	10	12.4
Be^{2+}	1	20.3	500	10.4	Zr^{4+}	0.02	54.3	10	22.1
Mg^{2+}	1	20.0	500	9.9	Th^{4+}	0.02	20.1	10	12.1
Ca^{2+}	1	19.9	500	9.9	Th^{4+}	—	—	10[a]	10.0
Sr^{2+}	1	19.9	500	10.0	V(V)	0.02	22.5	10	12.5
Ba^{2+}	1	20.3	500	10.0	Cr^{3+}	1	20.7	50	10.3
Al^{3+}	0.2	20.1	—	—	Mo(VI)	0.04	20.0	20	9.9
Ga^{3+}	0.02	25.2	10	13.5	W(VI)	0.5	19.5	100	9.7
In^{3+}	0.5	20.6	10	11.4	UO_2^{2+}	1	20.0	500	10.5
Sn^{4+}	0.02	24.2	10	10.3	Mn^{2+}	1	19.7	500	9.9
Pb^{2+}	1	20.1	100	10.2	Fe^{3+}	—	—	10	13.5
As(V)	1	19.5	100	10.0	Co^{2+}	1	19.9	50	10.3
Sb^{3+}	0.1	20.8	100	9.8	Ni^{2+}	1	19.7	10	10.5
Bi^{3+}	0.02	23.7	10	11.9	Rh^{3+}	1	20.2	100	9.9
Cu^{2+}	1	20.0	10	12.1	Pd^{2+}	0.5	20.7	20	10.4
Cu^{2+}	—	—	20[a]	9.9	Ir^{4+}	1	19.0	250	9.8
Au^{3+}	1	20.4	500	9.9	Pt(IV)	1	20.3	500	10.0
Zn^{2+}	1	20.0	250	10.5	F^-	0.1	19.5	10	6.6
Cd^{2+}	1	19.8	500	10.0	PO_4^{3-}	10	19.1	1000	9.8
Hg^{2+}	0.5	20.6	500	10.2	SO_4^{2-}	10	20.0	1000	9.6
Sc^{3+}	0.1	20.1	10	17.2	Oxalate	0.02	19.4	10	9.0
Y^{3+}	1	20.0	10	10.3	Tartrate	10	19.9	1000	10.2
La^{3+}	1	19.9	500	10.3	Citrate	10	19.8	1000	10.0

A: Effect on iron(III) determination (20 μg of iron(III) was taken). *B*: Effect on aluminium determination (10 μg of aluminium was taken). a) 2 cm³ of 1 mmol dm⁻³ EDTA solution was added after color development.

lanthanoids, manganese(II), cobalt, and nickel did not interfere, even if they were present at a concentration of 50 times that of iron(III). With regard to the anions, 500 fold amounts of tartrate, citrate, phosphate, or sulfate did inotnterfere. Gallium, tin(IV), bismuth(III), zirconium, and vanadium(V), however, interfered seriously. For the aluminium determination, gallium, indium, bismuth(III), copper, scandium, titanium(IV), zirconium, thorium, vanadium(V), iron(III), fluoride, and oxalate interfered seriously, but copper and thorium could be masked partly by the addition of 2 cm^3 of 1 mmol dm^{-3} EDTA solution at room temperature after color development.

Consecutive Determination of Iron(III) and Aluminium. Iron(III) interferes with the aluminium determination at pH 2.6 by the formation of iron(III)–SMXB complex, giving a positive error, but it can be determined at pH 1.3 without interference from aluminium. Utilizing these facts, the consecutive determination of iron(III) and aluminium has also been studied. The procedure for the determination is as follows.

The sample solution containing iron(III) and aluminium is divided equally. In one solution, the absorbance of the iron(III) complex alone is measured at 580 nm by using a recommended procedure for iron(III). In the other, the sum of the absorbances of the iron(III) and aluminium complexes is measured at 555 nm by using a recommended procedure for aluminium, by adding 5 cm^3 of reagent solution. From these data, the contents of both iron(III) and aluminium in the original samplesolution can be determined by using the following equations:

$$C_{\mathrm{Fe}} = 2 \times \frac{A_{580}}{a_{580}^{\mathrm{Fe}}}, \qquad C_{\mathrm{Al}} = 2 \times \frac{A_{555} - (a_{555}^{\mathrm{Fe}}/a_{580}^{\mathrm{Fe}})A_{580}}{a_{555}^{\mathrm{Al}}},$$

where C_{Fe} and C_{Al} are the contents of iron(III) and aluminium, and A_{580} and A_{555} are the absorbances at 580 and 555 nm, respectively. Further, a_{580}^{Fe} and a_{555}^{Fe} are the absorbances per 1 microgram of iron(III) at 580 and 555 nm respectively, and a_{555}^{Al} is that of aluminium at 555 nm. As shown in Table 2, satisfactory results were obtained with the solutions contain-

TABLE 2. CONSECUTIVE DETERMINATION OF IRON(III) AND ALUMINIUM

Taken (μg) Fe(III)	Taken (μg) Al	Found (μg) Fe(III)	Found (μg) Al
4	4	4.0	3.9
4	20	4.0	20.0
4	30	4.0	31.0
20	20	20.6	20.4
20	30	20.0	30.0
50	4	49.8	4.0
50	30	50.6	31.0

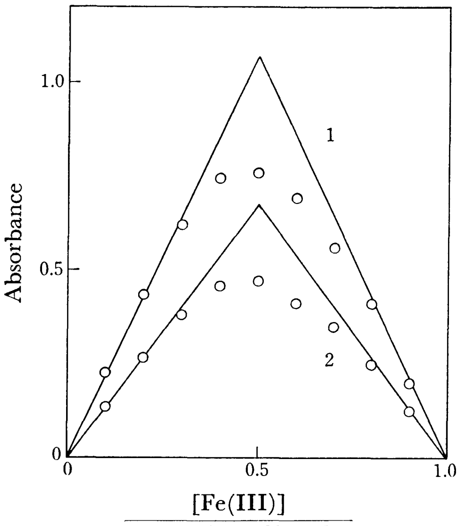

Fig. 3. Mole ratio of iron(III) complex determined by continuous variation method.
$[Fe(III)]+[SMXB]=7.16\times10^{-5}$ mol dm^{-3}, pH: 1.3, wavelength(nm)—1: 580, 2: 610.

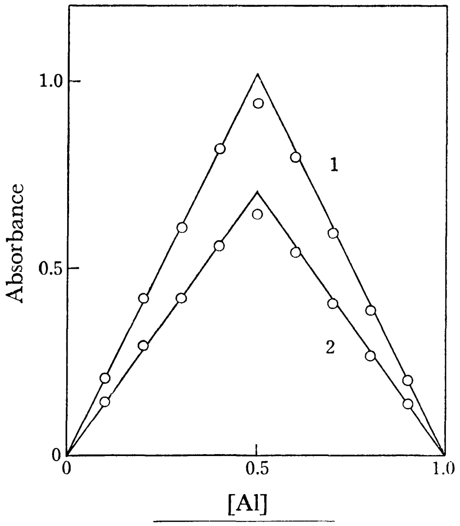

Fig. 4. Mole ratio of aluminium complex determined by continuous variation method.
$[Al]+[SMXB]=7.41\times10^{-5}$ mol dm^{-3}, dioxane: 10 cm^3, pH: 2.6, wavelength(nm)—1: 555, 2: 525.

ing 0.16—2.0 μg cm^{-3} of iron(III) and 0.16—1.2 μg·cm^{-3} of aluminium.

The Composition of the Complexes. The results obtained by the continuous variation method are shown in Figs. 3 and 4, from which it can be assumed that both iron(III) and aluminium formed the 1:1 complex with SMXB, though other iron(III) complexes may be formed at higher concentrations of iron(III). The same results were also obtained by the mole ratio method.

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