The Spectrophotometric Determination of Aluminum with Xylenol Orange[1]

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Various workers have proposed a variety of reagents for aluminum determination, including aluminon[2], hematoxylin[3], pontachrome blue black R[4], oxine[5], eriochrome cyanine R[6,7], quinalizarin[8], alizarin S[9], arsenoazo[10], cupferron[11], stilbazo[12], quercetin[13] and morin[14]. Of these reagents, the most promising one appears to be eriochrome cyanine R[15], which is sensitive for 0.004 μg. of aluminum per cm^2 for log $I_0/I=0.001$.

The present paper describes a new spectrophotometric method for the determination of aluminum, based on the highly sensitive color reaction of xylenol orange with aluminum in an acetate buffer solution. The development of the method includes a study of the effects of pH value, reagent concentration and foreign ions. The composition of the complex is also discussed.

It is found that, for aluminum, xylenol orange is a more sensible reagent than eriochrome cyanine R.

Experimental

Reagents. — An aluminum stock solution was prepared by dissolving aluminum nitrate crystals of analytical grade in dilute nitric acid; it was then standardized against a standard EDTA solution[16]. It was diluted with water to desired concentrations.

Acetic acid and sodium acetate solutions were used for all pH adjustments.

Apparatus. — Spectrophotometric measurements

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1) Presented at the Tohoku Branch Meeting of the Chemical Society of Japan, Yonezawa, October, 1961.

2) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis", D. Van Nostrand Company, Inc., New York (1949), p. 248.

3) H. W. Knudson, V. W. Meloche and C. Juday, *Ind. Eng. Chem., Anal. Ed.*, **12**, 715 (1940).

4) A. Weissler and C. E. White, ibid., **18**, 530 (1946).

5) C. H. R. Gentry and L. G. Sherrington, *Analyst*, **71**, 432 (1946).

6) F. Alten, W. Weiland and E. Knippenberg, *Z. anal. Chem.*, **96**, 91 (1934).

7) U. T. Hill, *Anal. Chem.*, **20**, 1117 (1948); **31**, 429 (1959).

8) I. M. Kolthoff, *Chem. Week-blad*, **24**, 447 (1927).

9) J. H. Yoe and W. L. Hill, *J. Am. Chem. Soc.*, **50**, 748 (1928).

10) V. I. Kuznetsov and R. B. Golubstova, *Zavodskaya Lab.*, **72**, 406 (1956).

11) L. de Brouckere and E. Belche, *Bull. soc. chim. Belg.*, **36**, 288 (1927).

12) M. Jean, *Anal. Chim. Acta*, **10**, 526 (1954).

13) A. L. Daxydov and U. S. Devekki, *Zavodskaya Lab.*, **57**, 134 (1941).

14) C. E. White and C. S. Lowe, *Ind. End. Chem., Anal. Ed.*, **12**, 229 (1940).

15) D. Blair, K. Power, D. L. Griffiths and J. H. Wood, *Talanta*, **7**, 80 (1960).

16) K. Ueno, "Chelatometric Titration", (in Japanese), Nankodo, Tokyo (1960), p. 207.

were made with a Hitachi Model EPV-2 spectrophotometer, using 1 cm. glass transmission cells.

All experiments were carried out at 25±0.5°C.

Procedure. — To an aliquot portion of the aluminum nitrate solution in a 50 ml. Erlenmeyer flask, 10 ml. of a pH 3.4 buffer solution and 2 ml. of a 1×10^{-3} M xylenol orange solution were added. The solution was heated on a boiling water bath for a few minutes, cooled with water to room temperature, and transferred to a 25 ml. volumetric flask. The volume of the content was then made up to the mark with water. After the solution had been kept for about 15 min. in a 25°C thermostat, the absorbance of the solution was measured at 536 mμ using a reagent blank.

Results and Discussion

Absorption Spectra. — Figure 1 shows the absorption spectra of solutions containing 6.2 μg. of aluminum with xylenol orange added in various amounts up to 6×10^{-5} M. These spectra show an isosbestic point at 536 mμ. The absorption maximum at about 555 mμ shifted slightly towards a shorter wavelength, and the extinction coefficient at this wavelength decreased, with increasing amounts of xylenol orange. From these observations it is expected that, by adding an xylenol orange solution in excess, a new complex other than one with an absorption maximum at about 555 mμ may be formed. The optimum pH range for the color development was found to be 3.4±0.1.

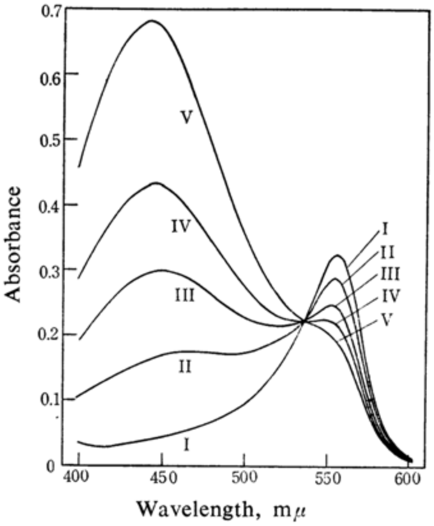

Fig. 1. Absorption spectra of aluminum-xylenol orange at pH 3.4.
Al: 6.2 μg.
XO concn.: I, 1×10^{-5} M; II, 2×10^{-5} M; III, 3×10^{-5} M; IV, 4×10^{-5} M; V, 6×10^{-5} M

Effect of Heating. — As in the case of the titration of aluminum with EDTA[17], the color reaction of xylenol orange with aluminum was very slow at room temperature. About 4 hr. were required for complete color development. When a solution containing xylenol orange and aluminum was heated on a boiling water bath, however, the reaction was greatly accelerated, and the maximum color development was obtained within only a few minutes.

Stability of Color.—The absorbance of the solution of the aluminum-xylenol orange complex at 555 mμ decreased gradually with the time of standing. About 10% of its intensity was diminished within the first 2 hr., and about 2% within an additional 2 hr. However, the absorbance at the isosbestic point of 536 mμ remained constant for several hr.

The Effect of Reagent Concentration. — In order to study the effect of the concentration of xylenol orange, a series of absorbances was measured under various concentrations of xylenol orange, using water and reagent blanks of the same concentration as points of reference. At 555 mμ, as is shown in Fig. 2, the maximum absorbance is obtained with a molar ratio of the reagent to aluminum of 1:1. Above this ratio, the additional reagent decreases the absorbance greatly, showing that a complex other than a 1:1 complex may be formed in this region. However, the absorbance at the isosbestic point of 536 mμ is not affected by the amounts of xylenol orange. In the actual aluminum determination, therefore, 2 ml. of a 1×10^{-3} M reagent solution were used, and the absorbance measurements were made at 536 mμ.

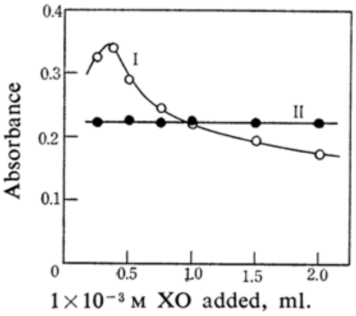

Fig. 2. Effect of reagent concentration.
Al: 6.2 μg. I: 555 mμ II: 536 mμ

Calibration.—Measurements of the absorbance were made with a number of colored solutions containing varying amounts of aluminum. Figure 3 shows that Beer's law is obeyed over the range 5 to 25 μg. of aluminum. The sensitivity is 0.001 μg. of aluminum per cm² for $\log I_0/I=0.001$. The molar extinction

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[17] K. Ueno, ibid., p. 205.

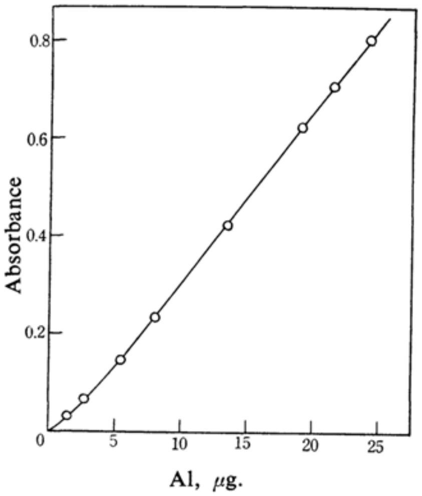

Fig. 3. Calibration curve at 536 mμ.

coefficient is 21100. Of the reagents proposed for aluminum determination, xylenol orange seems to be the most sentitve.

The Effect of Anions.—The effect of 15 cations was studied, along with that of the corresponding sodium salts. Chloride and nitrate ions did not interfere. Large amounts of sulfate, phosphate, tartrate and citrate reduced the absorbance considerably. Such anions as fluoride, nitrilotriacetic acid (NTA) and EDTA could form more stable complexes with aluminum than xylenol orange, giving very low results.

The Effect of Cations.—In order to test the effect of diverse cations upon the aluminum determination, absorbance measurements were made for the solutions containing 13.0 μg. of aluminum and 0.5 μmol. of several cations. The results are presented in Table I. Some of cations tested produce a red color, giving too high results. This is the only weak point in applying the present method to aluminum determination. However, the interferences from some cations such as chromium and nickel can be tolerably eliminated by shortening the time of heating for color development and prolonging the time of standing.

The Composition of the Complex.—As has been suggested above, two complexes which differ in composition are probably in equilibrium with each other. From Fig. 2, one of them seems to be a 1 : 1 complex.

TABLE I. EFFECT OF CATIONS ON ALUMINUM DETERMINATION

Aluminum taken, 13.0 μg.
Cation added, 0.5 μmol.

Cation	Al found, μg.	Deviation, μg.
Barium(II)	12.7	−0.3
Bismuth(III)	21.7	+8.7
Calcium(II)	12.6	−0.4
Cadmium(II)	12.8	−0.2
Cerium(III)	14.1	+1.1
Cobalt(II)	13.5	+0.5
Chromium(III)	18.2	+5.2
Copper(II)	13.2	+0.2
Iron(III)	31	+18
Mercury(II)	13.2	+0.2
Lanthanum(III)	14.0	+1.0
Magnesium(II)	12.8	−0.2
Manganese(II)	13.1	+0.1
Neodymium(III)	15.7	+2.7
Nickel(II)	16.0	+3.0
Lead(II)	12.8	−0.2
Palladium(II)	13.7	+0.7
Tin(II)	14.9	+1.9
Thorium(IV)	33	+20
Titanium(IV)	20.7	+7.7
Thallium(III)	13.3	+0.3
Uranium(VI)	12.8	−0.2
Vanadium(IV)	21.7	+8.7
Yttrium(III)	20.6	+7.6
Zinc(II)	13.9	+0.9
Zirconium(IV)	20.5	+7.5

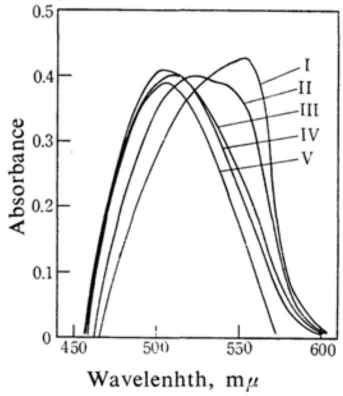

Fig. 4. Absorption spectra at various pH values.
Al: 13 μg. I, pH 2.0∼2.5; II, pH 3.0; III, pH 4.0; IV, pH 4.5; V, pH 5.5

In order to observe the spectral changes on varying pH values, absorption curves for the aluminum complex were prepared at various pH values, using the reagent blanks of the same concentration and pH value. The results are shown in Fig. 4. The absorption maximum at 555 mμ arising at pH 2 to 2.5 is shifted towards a shorter wavelength with an increase in the pH value; at pHs 3.0, 4.0 and 4.5 to 5.5, the maxima are found at about 520, 510 and 505 mμ respectively. These shifts in absorption maximum mean that probably two species of absorbing entity are involved; the one is a complex having an absorption maximum at about 555 mμ, which is formed at pH below 3, while the other is one having a maximum at about 505 mμ, which is formed at pH above 4.5.

Figures 5 and 6 indicate the absorption spectra at pHs 2.0 and 5.0 respectively. In both cases, the spectra were prepared with solutions containing 0.5, 1 and 2 parts of xylenol orange to one part of aluminum, using water as a reference. No change in the position of the absorption maximum is observed, when 1 : 2 and 1 : 1 are the molar ratios of xylenol orange to aluminum. Almost the same position of the absorption maximum is obtained at pH 2.0, even if the ratio is changed to 2 : 1. At pH 5.0, however, as is shown in Fig. 6, the absorption maximum at 555 mμ fades away to give a new maximum at a shorter wavelength when the ratio is changed to 2 : 1. The appearance of this new band means that, in a higher pH region, a new complex is also formed by adding xylenol orange in a slight excess.

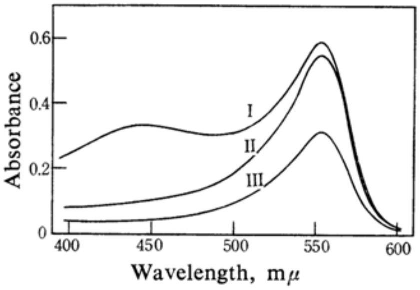

Fig. 5. Absorption spectra at pH 2.0.
I: XO : Al=2 : 1
II: XO : Al=1 : 1
III: XO : Al=1 : 2

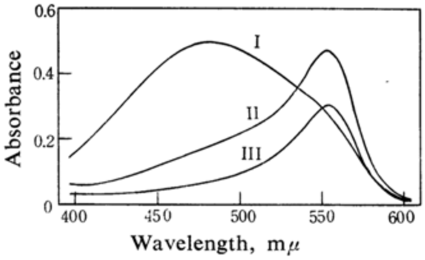

Fig. 6. Absorption spectra at pH 5.0.
I: XO : Al=2 : 1
II: XO : Al=1 : 1
III: XO : Al=1 : 2

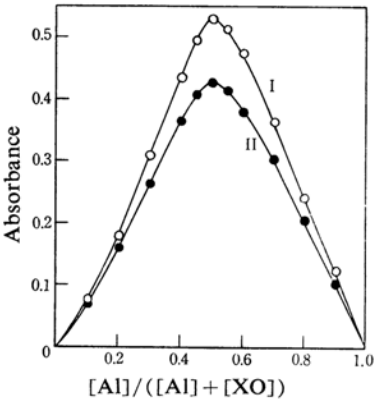

Fig. 7. Method of continuous variations at pH 2.0.
$[\mathrm{Al}]+[\mathrm{XO}]=4\times10^{-5}$ M
I: 545 mμ, II: 535 mμ

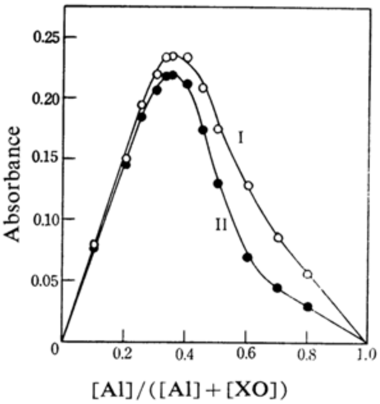

Fig. 8. Method of continuous variations at pH 5.
$[\mathrm{Al}]+[\mathrm{XO}]=4\times10^{-5}$ M
I: 505 mμ, II: 495 mμ

Figures 7 and 8 show plots of the results obtained by applying the method of continuous variations. These results indicate that only a 1 : 1 complex is formed at pH 2.0 and a 1 : 2 complex at pH 5.0. Although the data are not, because of the large corrections for the absorption of xylenol orange, precise enough to permit a further interpretation of the plots in Fig. 8, it is possible to consider that a small amount of 1 : 1 complex is also formed, even at pH 5.0.

From Figs. 5 to 8, it may be concluded that the complex formed at pH less than 3 has a different composition from one formed in a higher pH region. Namely, one of them has 1 : 1 as the ratio of the reagent to aluminum, and the other is a mixture of 1 : 1 and 1 : 2 complexes. It seems that formation of the 1 : 1 complex gradually diminishes with increasing pH value, whereas the 2 : 1 complex increases with pH. Similar relations were also observed for gallium- and thallium-xylenol orange complexes[18].

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[18] M. otomo, unpublished. (Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.)

Summary

Aluminum reacts with xylenol orange in a slightly acidic solution to form two red complexes which are in equilibrium with each other. At pH 3.4±0.1, Beer's law is obeyed up to an aluminum concentration of 1.0 p.p.m. in 1 cm. absorption cells. The absorbance was measured at the isosbestic point of 536 mμ. The molar extinction coefficient was found to be 21100. This method seems to be the most favorable one for aluminum determination if the aluminum is first separated from any interfering ions. The composition of the complexes has also been discussed.

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