BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1721—1724 (1966)

Studies of Calcichrome as a Spectrophotometric Reagent. IV. A New Spectrophotometric Method for the Determination of Aluminum with Calcichrome and Its Basic Study*

By Hajime ISHII and Hisahiko EINAGA

Central Research Laboratory, Onoda Cement Co., Ltd., Koto-ku, Tokyo

(Received December 7, 1965)

It has been found that Calcichrome forms a stable complex with aluminum; the reaction has been studied spectrophotometrically in order to find the optimum conditions for the determination of aluminum. The aluminum-Calcichrome complex is formed gradually at about pH 6; its composition has been found to be 1 to 1. The complex has two absorption maxima, at approximately 312 and 560 mμ, when measured against water. On the other hand, two absorption maxima were found, at approximately 317 and 620 mμ, in the curve obtained as the difference between Calcichrome and its aluminum complex. A linear relationship was noticed between the concentration of aluminum and the absorbance under the conditions recommended. The molar extinction coefficients of the complex at 317 and 620 mμ were 11500 and 7200. and the sensitivities were 2.3×10^{-3} and 3.7×10^{-3} μg. Al/cm^2 respectively, which correspond to $\log(I_0/I)=0.001$. Some other metals, such as copper(II), iron(III), titanium(IV), vanadium(V), and zirconium(IV), interfere with the determination.

The present authors have found that Calcichrome, reported by Close and West[1] to be a reagent useful in the determination of calcium, forms stable complexes with copper(I and II) and iron(III); they have already reported new spectrophotometric methods for the determination of copper[2,3] and iron[4] on the basis of the formation of each complex. Furthermore, the present authors have recently discovered that this reagent also forms a stable complex with aluminum. The present paper will describe a direct spectrophotometric method for the determination of aluminum with Calcichrome and the results of its basic study.

Experimental

Reagents.—*Calcichrome Solution.* — A Calcichrome solution (2×10^{-4} M) was prepared by dissolving 0.1982 g. of Calcichrome in distilled water and by then diluting the mixture to 1 l. The Calcichrome used in this study was synthesized and purified by the method described in an earlier paper.[3]

Standard Aluminum(III) Solution.—A standard aluminum solution corresponding to 1×10^{-2} mol./l. of aluminum was prepared by dissolving 4.744 g. of aluminum potassium sulfate in distilled water, then adding small amounts of sulfuric acid to prevent any possible hydrolysis and diluting the mixture to 1 l. Working solutions of aluminum were prepared from this solution by dilution.

Buffer Solutions.—Buffer solutions were prepared by mixing 1 M acetic acid and 1 M sodium acetate in the ratios required.

Apparatus.—A Hitachi automatic recording spectrophotometer, model EPS-2, and a Hitachi spectrophotometer, model 139, were used, with 1 cm. matched cells, for obtaining absorption curves and for all the other absorbance measurements respectively. A Toa Dempa glass-electrode pH meter, model HM-5A, was used for all the pH measurements.

The Recommended Procedure for the Determination.—To a sample solution containing aluminum in a 25-ml. volumetric flask, 5 ml. of the Calcichrome solution and 5 ml. of a buffer solution (pH 6.0) are added. The solution is diluted with distilled water to the mark. After the solution has stood for 30 min., the absorbance of the solution is measured at 620 mμ against a reagent blank treated in a similar manner.

Results and Discussion

Absorption Curves.—From the results of preliminary experiments, it was found that Calcichrome forms a stable bluish-violet complex with aluminum in a neutral and/or a weak acidic medium. The ultraviolet and visible absorption curves of the complex at pH 6.0 are shown in Fig. 1, from which it will be found that the complex has two absorption maxima in the ultraviolet (λ_{max} 312 mμ) and visible (λ_{max} 560 mμ) regions, as may be seen from curve I obtained against water. On the other hand, in the curve III (the apparent absorption curve), which is obtained as the difference between Calcichrome and its aluminum complex,

*1 Presented at the 14th Annual Meeting of the Japan Society for Analytical Chemistry, Kyoto, November, 1965.

1) R. A. Close and T. S. West, *Talanta*, **5**, 221 (1960).
2) H. Ishii and H. Einaga, This Bulletin, **38**, 1416 (1965).
3) H. Ishii and H. Einaga, ibid., **39**, 1154 (1966).
4) H. Ishii and H. Einaga, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **87**, 440 (1966).

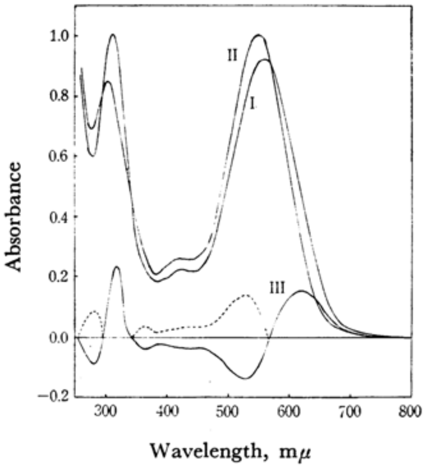

Fig. 1. Absorption spectra of Al(III)-Calcichrome complex.
Calcichrome: 4×10^{-5} mol./l.
Aluminum: 2.4×10^{-5} mol./l.
I: Al(III)-Calcichrome complex } Reference: water
II: Calcichrome alone }
III: Difference between curves I and II (Parts under the abscissa were reversed to the positive side (as dotted line) for clearity.)

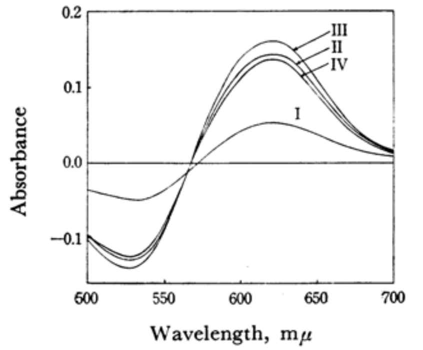

Fig. 2. Apparent absorption spectra of Al(III)-Calcichrome complex.
Calcichrome: 4×10^{-5} mol./l.
Aluminum: 2.4×10^{-5} mol./l.
Reference: Reagent blank
I: pH 4.3, II: pH 5.4, III: pH 6.0, IV: pH 6.3

two absorption maxima are found, at approximately 317 and 620 mμ. Figure 2 shows the apparent absorption curves of the complex at various pH values, from which it may be seen that the maximum absorption wavelength does not vary with the pH value. Taking account of this fact and of those described in the following paragraph, one species of the complex is considered to be formed under the conditions studied.

The Effect of pH on the Color Development.—The effect of pH on the color development of the aluminum-Calcichrome complex was examined at 620 mμ, with the concentrations of aluminum

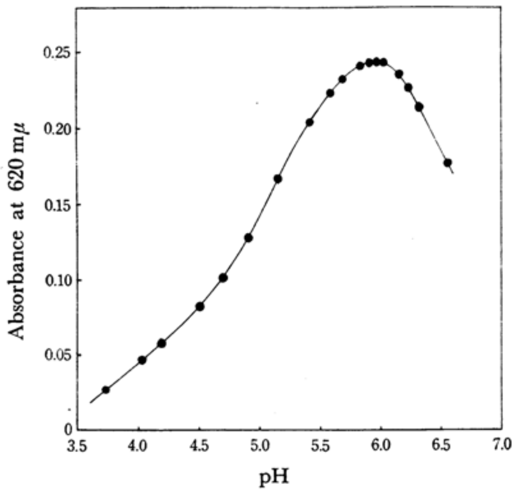

Fig. 3. Effect of pH on absorbance of the Al(III)-Calcichrome complex.
Calcichrome: 4×10^{-5} mol./l.
Aluminum: 4×10^{-5} mol./l.

and Calcichrome made to 4×10^{-5} mol./l. The results are shown in Fig. 3, from which it can be seen that the maximum color can be obtained at approximately pH 6, and that the pH range in which nearly the same absorbance can be obtained is rather narrow. Therefore, the pH should be carefully controlled in the determination of aluminum.

The Stability of the Color.—The color of the aluminum-Calcichrome complex develops gradually at room temperature; the full color is obtained 20 min. after the reagent is added. The time required to reach the full color can be, however, shortened remarkably by heating the solution to about 90°C. The color, once developed to the full, is very stable, and there is no change in absorbance over a period of 24 hr. Figure 4 shows the effect of the standing time on the absorbance.

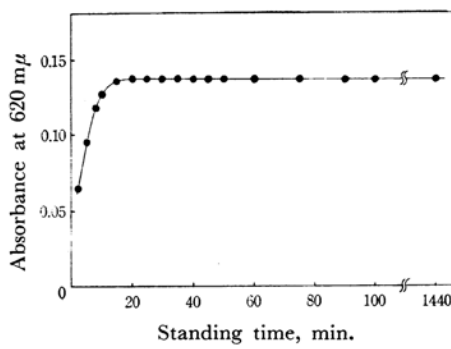

Fig. 4. Effect of standing time.
Calcichrome: 4×10^{-5} mol./l.
Aluminum: 2×10^{-5} mol./l.
pH: 6.0

The Effect of the Amount of Calcichrome.—The effect of the reagent concentration on color development was next examined, with the concentration of aluminum kept constant at 2×10^{-5} mol./l., with the pH values of the solutions at 6.0, and with the absorbance measurements carried out at 620 mμ. The results are shown in Fig. 5, from which it may be noticed that approximately a two-fold excess of the reagent over the aluminum concentration is necessary to obtain the maximum color intensity.

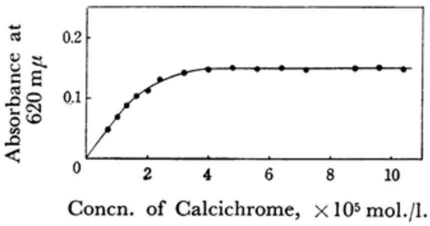

Fig. 5. Effect of amount of Calcichrome.
Aluminum: 2×10^{-5} mol./l.
pH: 6.0
Reference: Reagent blank

The Relationship between the Concentration of Aluminum and the Absorbance.—A linear relationship was found between the concentration of aluminum and the absorbance. The range of the aluminum concentration in which the linearity was noticed was, however, dependent upon the Calcichrome concentration; linearity was noticed up to the molar ratio of aluminum to Calcichrome of about 0.8. Figure 6 shows calibration curves for aluminum at 620 and 317 mμ. The molar extinction coefficient and the sensitivity which corresponds to $\log(I_0/I)=0.001$ are summarized in Table I. As may be seen from Fig. 6 and Table I, approximately 1.6 times as much sensitivity can be obtained when the

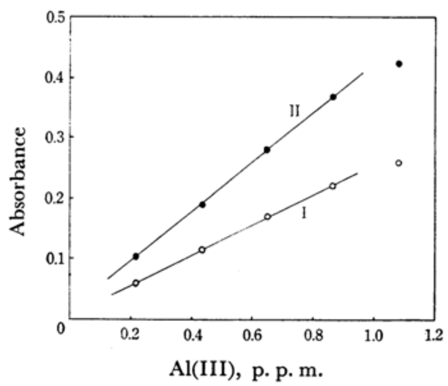

Fig. 6. Calibration curves.
Calcichrome: 4×10^{-5} mol./l.
pH: 6.0
Reference: Reagent blank
I: at 620 mμ, II: at 317 mμ

TABLE I. THE MOLAR EXTINCTION COEFFICIENT AND THE SENSITIVITY

Wavelength mμ	Molar extinction coefficient	Sensitivity
620	7200	3.7×10^{-3} μg. Al/cm^2
317	11500	2.3×10^{-3} μg. Al/cm^2

TABLE II. EFFECT OF DIVERSE IONS
Al taken: 0.62 p. p. m.

Diverse ion	p. p. m.	Al found p. p. m.	Relative error %
Ba(II)	5	0.62	± 0
Ca(II)	5	0.62	± 0
Cd(II)	5	0.62	± 0
Co(II)	1	0.63	+ 1.6
	4	0.65	+ 4.8
Cr(III)	0.1	0.59	− 4.8
	0.2	0.57	− 8.1
	0.4	0.52	−16.1
Cr(VI)	4	0.62	± 0
Cu(II)	0.1	0.62	± 0
	0.3	0.65	+ 4.8
	0.5	0.70	+12.9
Fe(III)	0.01	0.65	+ 4.8
	0.03	0.67	+ 8.1
	0.05	0.67	+ 8.1
	0.1	0.50	−19.4
Hg(II)	1	0.64	+ 3.2
	2	0.67	+ 8.1
	4	0.70	+12.9
Mg(II)	0.5	0.62	± 0
	1	0.57	− 8.1
Mn(II)	5	0.62	± 0
Ni(II)	0.1	0.64	+ 3.2
	0.3	0.65	+ 4.8
	0.5	0.67	+ 8.1
Pb(II)	5	0.62	± 0
Ti(IV)	0.3	0.67	+ 8.1
	0.5	0.69	+10.1
	1.0	0.72	+16.1
	2.0	0.62	± 0
	4.0	0.50	−19.4
V(V)	0.1	0.67	+ 8.1
	0.3	0.68	+ 9.7
	0.5	0.72	+16.1
Zn(II)	5	0.62	± 0
Zr(IV)	0.01	0.64	+ 3.2
	0.05	0.62	± 0
	0.1	0.61	− 1.6
	0.5	0.59	− 4.8
	1.0	0.57	− 8.1
Cl^-	100	0.62	± 0
$C_2O_4^{2-}$	0.2	0.61	− 1.6
	0.5	0.58	− 6.5
	1.0	0.55	−11.3
NO_3^-	100	0.62	± 0
SO_4^{2-}	100	0.62	± 0
$S_2O_3^{2-}$	100	0.61	− 1.6

absorbance of the solution is measured at 317 mμ as when it is measured at 620 mμ, however, the latter wavelength was employed in the recommended procedure because it seems to be more convenient than the former.

The Effect of Diverse Ions.—The effect of diverse ions on the determination of aluminum was examined at pH 6.0. The results are summarized in Table II. From this it can be concluded that cobalt(II), chromium(III), copper(II), iron(III), mercury(II), magnesium(II), nickel(II), titanium(IV), vanadium(V), and zirconium(IV) interfere; this is considered to be due to the formation of their complexes with Calcichrome. The tendency for a negative error to be given with increasing amounts of such cations as iron(III), titanium(IV), and zirconium(IV) is probably to be attributed to the easier complex formation of Calcichrome with these cations than that with aluminum, and to the diminution of the effective amounts of Calcichrome for complexing with aluminum. The interference of oxalate is probably due to complex formation with aluminum.

The Composition of the Complex.—Attempts to determine the composition of the complex were carried out by two methods; the continuous variation method and the mole ratio method. These attempts were made at pH 6.0, and the absorbance measurements were made at three wavelengths, 520, 605, and 620 mμ. Both methods revealed that aluminum forms a 1 to 1 complex with Calcichrome. As an example, the results obtained by the continuous variation method are shown in Fig. 7. The results by the mole ratio method, which are omitted to avoid duplication, are clear from Fig. 5.

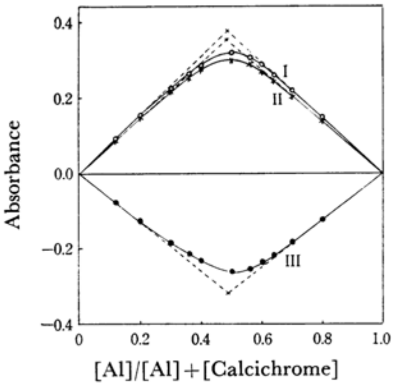

Fig. 7. Determination of mole ratio of Al(III)-Calcichrome complex.
[Al]+[Calcichrome] = 1×10^{-4} mol./l.
pH: 6.0
I: 620 mμ, II: 605 mμ, III: 520 mμ

Conclusion

It has been found that Calcichrome forms a 1 to 1 complex with aluminum, and a new spectrophotometric method for the determination of traces of aluminum has been proposed.