Fluorometric Determination of Aluminum and Gallium with Superchrome Garnet Y

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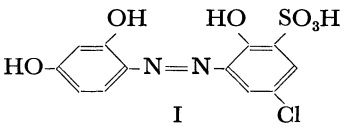
A sensitive fluorometric determination of aluminum and gallium with Superchrome Garnet Y was described. The reagent reacts with aluminum and gallium to form complexes with reddish yellow fluorescence of emission maximum at 562 and 565 nm respectively. Several conditions for the determination, such as the pH of the solution, the reagent concentration, the time of standing *etc.* were investigated, and the composition of the complexes was determined. The maximum fluorescence intensity of the aluminum complex was found at pH 5 (heated for 10 min at 50°C), and that of the gallium complex, at pH 3. The fluorescence were stable at least for 2 hr. By using Superchrome Garnet Y, 0.02—4 μg of aluminum and 0.5—30 μg of gallium in 25 m*l* solution could be determined. Scandium and indium also formed fluorescent complexes. Iron(III), cobalt(II), copper(II), zirconium(IV), vanadate(V), and chromate(VI) ions interfered with the determination.

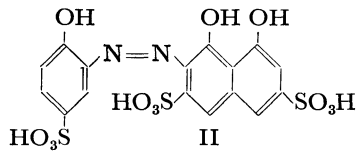
In the course of the investigation on the fluorometric determination of various metal ions with a series of *o,o'*-dihydroxyazo compounds, the author found that lumogallion [3-(2,4-dihydroxyphenylazo)-2-hydroxy-5-chlorobenzenesulfonic acid] (I) was a sensitive



I

reagent for the determination of aluminum and gallium, appliciable to the determination of aluminum in sea water.[1-3]

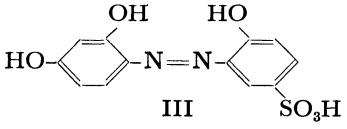
Mordant Blue 31 [2-(2-hydroxy-5-sulfophenylazo)-1, 8-dihydroxynaphthalene-3,6-disulfonic acid] (II) was



II

also a useful reagent for aluminum, gallium and scandium, and the fluorometric methods were proposed in a recent paper.[4]

Freeman and White[5] studied the configuration and the bond type of *o,o'*-dihydroxy azo compounds, which was favorable to form fluorescent metal complexes. According to their consideration, Superchrome Garnet Y [3-(2,4-dihydroxyphenylazo)-4-hydroxybenzenesulfonic acid] (III) seemed to be a very sensitive fluorescent reagent.



III

However, no quantitative investigation with this reagent has been carried out, except Powell and Saylor's research on the fluorometric determination of traces of fluoride using aluminum-Superchrome Garnet Y complex.[6]

The present author found that Superchrome Garnet Y was more sensitive than lumogallion for aluminum and gallium, and that scandium and indium also formed the fluorescent complexes, applicable to the fluorometric determination. In the present paper, the fundamental conditions for the determination of aluminum, gallium, scandium and indium with this reagent were described.

Reagent and Apparatus

Synthesis of Superchrome Garnet Y. 1-Amino-2-phenol-5-sulfonic acid dissolved in 6N hydrochloric acid was diazotized with an equivalent amount of sodium nitrite under ice-cooling. The cooled diazonium salt solution was added to resorcinol dissolved in about 6N sodium hydroxide under cooling below 5°C. The azo compound thus obtained was repeatedly recrystallized from 6N hydrochloric acid, and dried at room temperature in a desiccator on silica gel.

Solutions. Superchrome Garnet Y solution; 0.1 g of Superchrome Garnet Y was dissolved in redistilled water and diluted to a liter.

Standard solution of aluminum; 1.6803 g of alum was dissolved in water, and after 5 m*l* of concentrated hydrochloric acid was added, diluted to 100 m*l* with water. The stock solution was diluted with water to prepare a solution containing 1.00 μg of aluminum per m*l*.

Stock solution of gallium, scandium and indium were prepared by dissolving the 99.99%, 99.9%, and 99.99% pure oxides with 6N hydrochloric acid, respectively, and the standard solutions were prepared by suitable dilution from the stock solution.

Rhodamine B solution; 0.1 g of Rhodamine B was dissolved in water and diluted to 100 m*l*. The stock solution was diluted with water to make solutions containing 0.168 and 0.05 μg rhodamine B per m*l*. The former solution was sufficiently stable for several months, while the latter was unstable and must be freshly prepared every five days. These solutions were used as reference standards to adjust the sensitivity of the instrument.

All other chemicals used in the present work were special grade. Ethanol, hydrochloric acid and ammonia were dis-

1) Y. Nishikawa, K. Hiraki, K. Morishige, and T. Shigematsu, *Bunseki Kagaku*, **16**, 692 (1967).

2) Y. Nishikawa, K. Hiraki, K. Morishige, A. Tsuchiyama, and T. Shigematsu, *ibid.*, **17**, 1092 (1968).

3) T. Shigematsu, Y. Nishikawa, K. Hiraki, and N. Nagano, *ibid.*, **19**, 551 (1970).

4) K. Hiraki, This Bulletin, **45**, 789 (1972).

5) D. C. Freeman and C. E. White, *J. Amer. Chem. Soc.*, **78**, 2678 (1956).

6) W. A. Powell and J. H. Saylor, *Anal. Chem.*, **25**, 960 (1953).

tilled until the fluorescence disappeared. Redistilled water was used throughout the procedures.

Apparatus. Fluorescence spectra and the intensity were measured with a Hitachi spectrophotometer, Model G-3 (exciting source; 150 W Xenon lamp). A Hitachi-Horiba glass electrode pH meter, Model M-5, was used for the pH measurements.

Experimental

Fluorescence Spectra of the Metal Complexes of Superchrome Garnet Y. Superchrome Garnet Y reacted with aluminum, gallium, scandium, and indium to form complexes with orange fluorescence. Aluminum-Superchrome Garnet Y complex exhibited the excitation maxima at 365 and 485 nm and the fluorescence emission maximum at 562 nm; the gallium complex showed excitation maxima at 365 and 485 nm and the fluorescence maximum at 565 nm; the scandium complex had the excitation and the emission maximum at 482 and 575 nm respectively; and the indium complex, at 480 and 565 nm respectively. Spectra of Superchrome Garnet Y complexes are shown in Figs. 1 and 2.

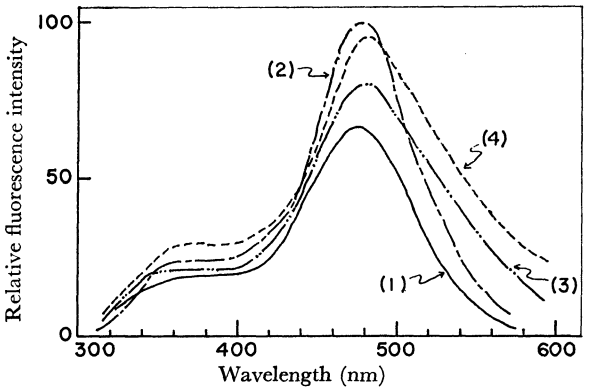


Fig. 1. Excitation spectra of aluminum, gallium, scandium and indium complexes.
(1): Al-Superchrome Garnet Y complex, emission spectrum measured at 562 nm; (2): Ga-Superchrome Garnet Y complex, emission spectrum measured at 565 nm; (3): Sc-Superchrome Garnet Y complex, emission spectrum measured at 575 nm; (4): In-Superchrome Garnet Y complex, emission spectrum measured at 565 nm.

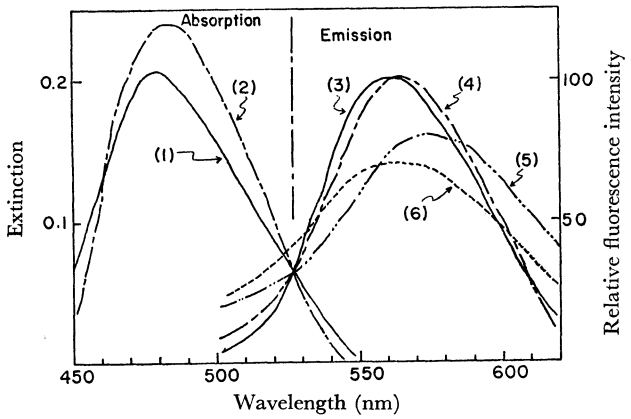


Fig. 2. Absorption and emission spectra of Superchrome Garnet Y complexes.
(1): Absorption spectrum of Al-Superchrome Garnet Y complex; (2): Absorption spectrum of Ga-Superchrome Garnet Y complex; (3): Emission spectrum of Al-Superchrome Garnet Y complex; (4): Emission spectrum of Ga-Superchrome Garnet Y; (5): Emission spectrum of Sc-Superchrome Garnet Y; (6): Emission spectrum of In-Superchrome Garnet Y complex.

Fluorescence Procedure for the Determination of Metals. *1) Aluminum*: To 15—20 m*l* of the sample solution containing 0.1—4 μg of aluminum were added 0.7 m*l* of 0.01% Superchrome Garnet Y and 2 m*l* of 20% ammonium acetate and the pH was adjusted to 5 with dilute hydrochloric acid or ammonia. The solution was diluted to 25 m*l* with water and then kept at 50°C for 10 min. After cooling, the fluorescence intensity was measured by using a Rhodamine B solution as the reference standard.

2) Gallium: To the sample solution containing 0.5—30 μg of gallium were added 0.8 or 1.7 m*l* of 0.01% reagent and 2 m*l* of 20% ammonium acetate and the pH was adjusted to 3. The solution was diluted to 25 m*l* and then the fluorescence intensity was measured.

3) Scandium and Indium: Scandium (5—40 μg) was determined by the same procedure as in the case of gallium, but the pH was adjusted to 5.5. Indium (5—30 μg) was determined in the case of the same manner as aluminum, but 2 m*l* of the reagent solution was used.

Results and Discussion

Effect of Time of Standing. At room temperature, the aluminum and the indium complex needed 120 minutes' standing until they showed the full fluorescence. If the solutions were heated at 50°C, the fluorescence intensity readily reached the maximum. The fluorescence of the gallium and the scandium complex was fully developed within a few minutes after the preparation of the solutions.

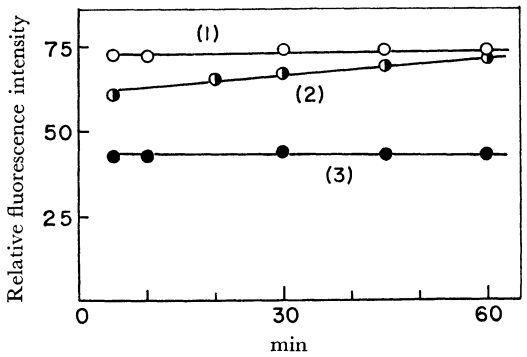


Fig. 3. Stability of fluorescence intensity of Superchrome Garnet Y complexes.
(1): Al 0.5 μg, digested at room temp., 485 nm/562 nm, fluorometer readings was setted at 40 div. with 0.168 μg rhodamine B/m*l* reference solution.
(2): Al 0.5 μg, digested at 50°C 10 min, 485 nm/562 nm, 40 div.
(3): Ga 5 μg, digested at room temp., 485 nm/565 nm, 20 div.

In all cases, the fluorescence was stable at least for 2 hr after reaching the maximum intensity. Figure 3 shows the stability of the fluorescent complexes of aluminum and gallium.

Effect of pH. The intensity of the fluorescence of metal complex was measured over a wide range of pH values. The results are shown in Fig. 4.

The aluminum and the indium complex showed maximum fluorescence intensity at pH 5, the scandium complex at pH 5.5, and the gallium complex showed

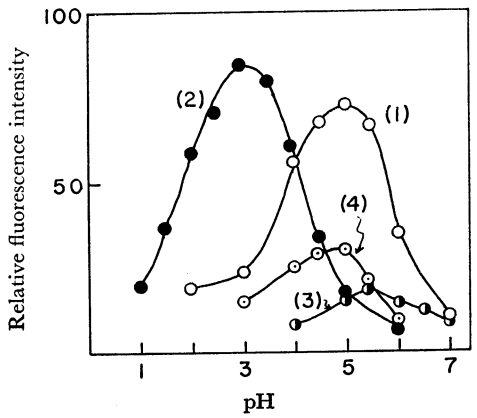


Fig. 4. Effect of pH on fluorescence intensity.
(1): Al 0.5 μg, 485 nm/562 nm, 40 div. *vis.* 0.168 μg Rhodamine B/m*l* standard solution:
(2): Ga 5 μg, 485 nm/565 nm, 40 div. *vis.* 0.168 μg Rhodamine B/m*l* standare solution;
(3): Sc 20 μg, 482 nm/575 nm, 60 div. *vis.* 0.168 μg Rhodamine B/m*l* standard solution;
(4): In 20 μg, 480 nm/565 nm, 60 div. *vis* 0.05 μg Rhodamine B standard solution.

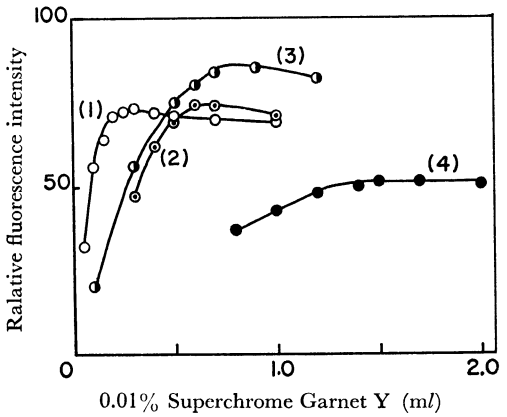


Fig. 5. Effect of reagent concentration.
(1): Al 0.5 μg, 485 nm/562 nm, 40 div. *vis.* 0.168 μg Rhodamine B standard solution;
(2): Al 3.5 μg, 365 nm/562 nm, 40 div. *vis.* 0.168 μg Rhodamine B standare solution;
(3): Ga 5 μg, 485 nm/565 nm, 40 div. *vis.* 0.168 μg Rhodamine B standard solution;
(4): Ga 25 μg, 485 nm/565 nm, 10 div. *vis.* 0.168 μg Rhodamine B standard solution.

the maximum in more acidic medium, near pH 3.

Effect of Concentration of Superchrome Garnet Y. The various amounts of Superchrome Garnet Y were added to the solutions containing 0.5 or 3.5 μg of aluminum, 5 or 25 μg of gallium, and the fluorescence intensity of the solution was measured at the optimum pH. Figure 5 shows the effect of the amounts of Superchrome Garnet Y on the fluorescence intensity.

The results indicated that 0.3 m*l* of 0.01% Superchrome Garnet Y solution was required for 0.5 μg of aluminum in 25 m*l* of solution and 0.7 m*l* for 3.5 μg of aluminum. In the case of gallium, 0.8 m*l* of the reagent solution was needed for up to 5 μg per 25 m*l* and 1.7 m*l* for 25 μg. For the determination of scandium and indium, 2 m*l* of 0.01% Superchrome Garnet Y solution was needed.

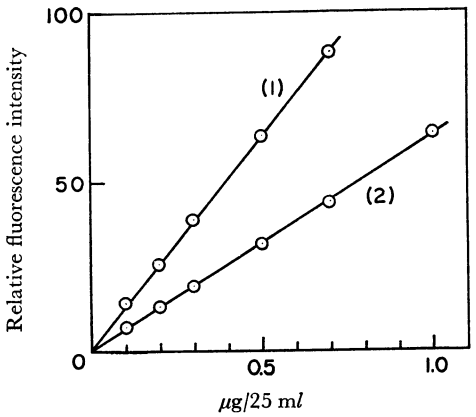


Fig. 6. Calibration curves for aluminum.
(1): 485 nm/562 nm, 40 div. *vis.* 0.168 μg Rhodamine B standard solution, 0.01% reagent solution 0.3 m*l*.
(2): 365 nm/562 nm, 30 div. *vis.* 0.168 μg Rhodamine B standard solution, 0.01% reagent solution 0.3 m*l*.

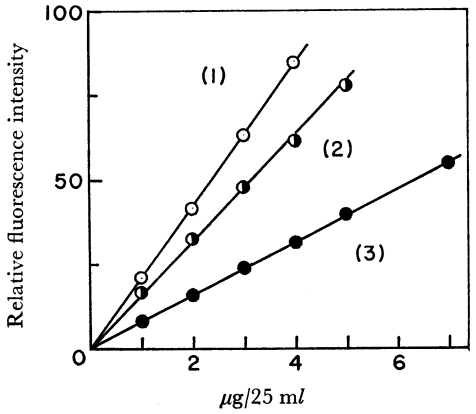


Fig. 7. Calibration curves for aluminum and gallium.
(1) Al: 485 nm/562 nm, 10 div. (0.168 μg Rhodamine B/m*l* standard solution), 0.01% reagent solution 0.7 m*l*.
(2) Ga: 485 nm/565 nm, 40 div. (0.168 μg Rhodamine B/m*l* standard solution), 0.01% reagent solusion 0.8 m*l*.
(3) Ga: 365 nm/565 nm, 30 div. (0.168 μg Rhodamine B/m*l* standard solution), 0.01% reagnet solution 0.8 m*l*.

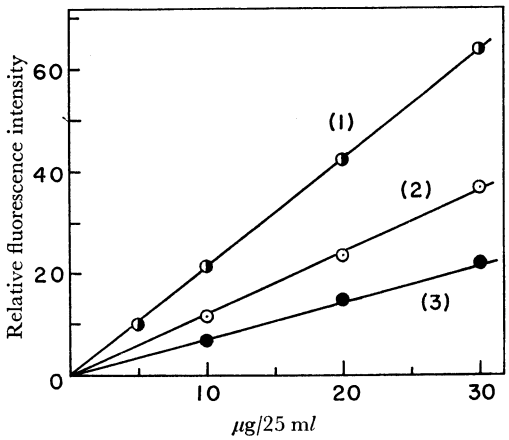


Fig. 8. Calibration curves for gallium, indium and scandium.
(1): Ga: 365 nm/565 nm, 10 div. (0.168 μg Rhodamine B/m*l* standard solution), 0.01% reagent solution 1.7 m*l*.
(2): In: 480 nm/565 nm, 60 div. (0.05 μg Rhodamine B/m*l* standard solution), 0.01% reagent solution 2 m*l*.
(3): Sc: 482 nm/575 nm, 60 div. (0.168 μg Rhodamine B/m*l* stadard solution), 0.01% reagent solution 2 m*l*.

Table 1. The conditions for the fluorometric determination of Al, Ga, Sc, and In

Ion	Al	Ga	Sc	In
Excitation wave length (nm)	365 485	365 485	482	480
λ_f max. (nm)	562	565	575	565
pH	5.0	3.0	5.5	5.0
Standing time	10 min., 50°C	10 min., room temp.	10 min., room temp.	10 min., 50°C
0.01%-reagent solution (ml)	0.3 0.7	0.8 1.7	2.0	2.0
Determinable range (μg/25 ml)	0.02—1.0 0.02—4.0	0.5—7.0 0.5—30	5—40	5—30
Fluorescence intensity at 60 div. per 1 μg	195	25.5	0.8	0.3
F. I. ratio {weight[a]	650	85	2.7	1
F. I. ratio {molar[b]	1463	494	1	10

a) This ratio was expressed in values relative to a fluorescence intensity of the indium complex for 1 μg In/25ml. (60 div., *vs.* 0.168 μg rhodamine B/ml)
b) This ratio was expressed in values relative to a fluorescence intensity of the scandium complex for 1 mol Sc/*l*. (60 div., *vs.* 0.168 μg rhodamine B/ml)

Calibration Curves. Figures 6, 7, and 8 show the calibration curves for aluminum, gallium, scandium and indium, respectively, which were obtained by the above-mentioned procedures. The sensitivity of the fluorometer was regulated by setting up the fluorescence of a standard Rhodamine B solution (0.168 μg/ml or 0.05 μg/ml) at an appropriate position of the reading (10—60 division). Aluminum, gallium, scandium, and indium can be determined in the following ranges with an average error of 3 percent; Al: 0.02—4 μg, Ga: 0.5—30 μg, Sc: 5—40 μg, In: 5—30 μg. A linear relationship exists between the fluorescence intensity and the metal ion concentration. The conditions for the fluorometric determination of these metal ions were summarized in Table 1.

For the determination of indium, 0.05 μg Rhodamine B per ml solution was used as the reference standard in order to raise the sensitivity of the fluorometer. Use of the dilute reference standard solution enabled the determination of aluminum, gallium, and scandium in lower concentrations, but the error was increased. The errors might be mainly due to two reasons; the lowering of the stability of the fluorometer resulting from the too high sensitivity, and the change of the concentration of Rhodamine B caused by the adsorption on the vessel wall that would be negligible in the concentrated standard.

Effect of Diverse Ions. The effects of 27 cations on the determination of aluminum and gallium were studied. The results are summarized in Table 2.

In the determination of aluminum, twentyfold amounts of cobalt(II), copper(II), iron(III), zirconium-

Table 2. Effect of diverse ions

Ion	Added as	(μg)	Al found (μg)[a]	Diverse ion added (μg)	Ga found (μg)[b]
Be^{2+}	$Be(NO_3)_2$	10	0.5	20	5.3
Mg^{2+}	$MgSO_4$	10	0.5	20	4.8
Ca^{2+}	$CaCl_2$	10	0.5	20	5.0
Cu^{2+}	$CuSO_4$	10	0.0	20	1.6
Zn^{2+}	$ZnSO_4$	10	0.4	20	5.0
Sr^{2+}	$Sr(NO_3)_2$	10	0.5	20	5.0
Cd^{2+}	$CdSO_4$	10	0.5	20	5.3
Co^{2+}	$CoCl_2$	10	0.1	20	4.1
Ni^{2+}	$Ni(NO_3)_2$	10	0.4	20	4.8
Sc^{3+}	$ScCl_3$	10	0.4	20	5.0
Ga^{3+}	$GaCl_3$	10	0.4	—	—
Y^{3+}	YCl_3	10	0.5	20	4.8
Eu^{3+}	$EuCl_3$	10	0.5	20	5.0
In^{3+}	$InCl_3$	10	0.5	20	5.0
La^{3+}	$LaCl_3$	10	0.5	20	5.0
Tl^{3+}	$TlCl_3$	10	0.5	20	5.0
Fe^{3+}	$FeCl_3$	10	0.0	10	0.5
Zr^{4+}	$Zr(SO_4)_2$	10	0.0	20	3.4
Sn^{2+}	$SnCl_2$	10	0.4	20	4.8
V^{5+}	NH_4VO_3	10	0.0	10	0.4
Cr^{6+}	K_2CrO_4	10	0.0	10	0.0
Se^{4+}	Na_2SeO_3	10	0.5	20	4.8
Mo^{6+}	$(NH_4)Mo_7O_{24}$	10	0.5	20	3.6
Mn^{2+}	$MnSO_4$	10	0.4	20	5.0
UO_2^{2+}	$UO_2(CH_3COO)_2$	10	0.4	20	5.0
Th^{4+}	$Th(NO_3)_4$	10	0.5	20	5.0
Al^{3+}	$AlCl_3$	—	—	10	+

a) 0.5 μg of aluminum was taken.
b) 5.0 μg of gallium was taken.

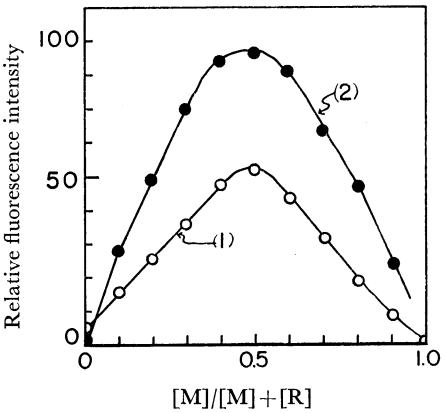


Fig. 9. Continuous variation method.
(1): M:Al, pH: 5.0, 485 mn/562 nm, 20 div. $[Al]+[R]=7.42\times10^{-5}$M
(2): M: Ga, pH: 3.0, 485 nm/565 nm, 30 div. $[Ga]+[R]=3.22\times10^{-4}$M

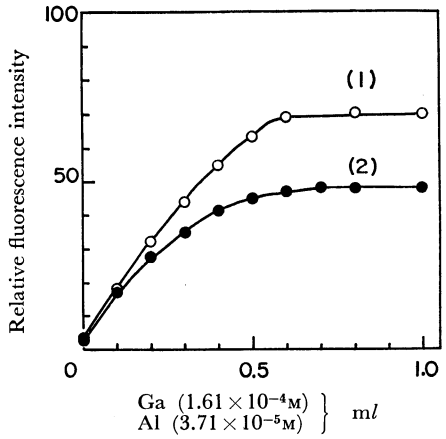


Fig. 10. Mole ratio method
(1): Al; [R]: 3.71×10^{-5}M 0.5 m*l*, 485 nm/562 nm, 60 div.
(2): Ga; [R]: 1.61×10^{-4}M 0.5 m*l*, 485 nm/562 nm, 30 div.

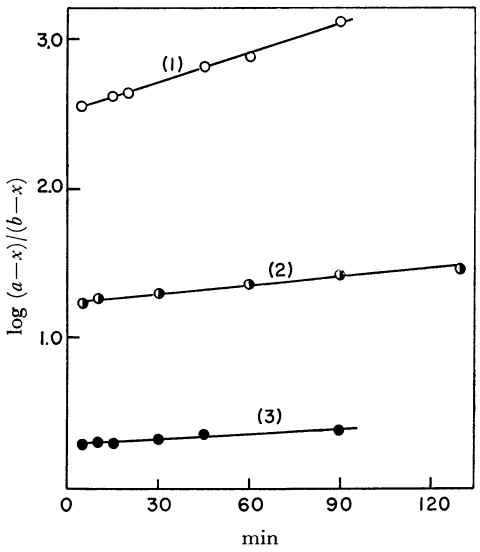


Fig. 11. Kinetics of chelate formation as indicated by fluorescence.
a is initial concentration of aluminum, *b* is initial concentration of Superchrome Garnet Y, and *x* is concentration of chelate as indicated by fluorescence.
(1) *a*: 10 μmol, *b*: 1 μmol;
(2) *a*: 1 μmol, *b*: 1 μmol;
(3) *a*: 1 μmol, *b*: 10 μmol'

(IV), vanadium(V), and chromate(VI) ions reduced the fluorescence intensity, but the following ions did not interfere; beryllium(II), calcium(II), cadmium(II), strontium(II), manganese(II), nickel(II), tin(II), magnesium(II), indium(III), gallium(III), scandium(III), lanthanum(III), yttrium(III), europium(III), thallium (III), zinc(II), selenium(IV), thorium(IV), molybdate (VI), and uranyl(VI) ions. In the determination of gallium, aluminum(III) gave positive error, and quadruple amounts of cobalt(II), copper(II), iron(III), zirconium(IV), vanadium(V), molybdate(VI), and chromate(VI) ions reduced the fluorescence, but other ions, presented in Table 1, did not interfere.

Determination of Metal to Ligand Ratio. The mole ratio of metal to ligand in the metal complexes of Superchrome Garnet Y was determined fluorometrically by the continuous variation method and the mole ratio method. Because the aluminum complex formed slowly at room temperature the metal to ligand ratio was also kinetically determined.

The results are shown in Figs. 9 (continuous variation method), 10 (mole ratio method) and 11 (kinetic method). Figures 9 and 10 indicate that both aluminum and gallium form the 1 : 1 complex. Figure 11 shows that the formation of the aluminum complex follows the second-order kinetics, and therefore, supports the above-mentioned composition.

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