Studies on the Fluorometric Analysis. (IV)

Fluorometric Determination of Gallium with 8-Hydroxyquinoline

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On the way to the systematic studies on the fluorescence and optical properties of metallo-oxinates, the authors found that gallium-oxinate emits a strong fluorescence (the luminescence band lies at 450~650mμ) when excited with the radiation of 365mμ-Hg line at room temperature. In this paper, a fluorometric method for the determination of gallium with 8-hydroxyquinoline was studied.

INTRODUCTION

E. B. Sandell[1] introduced 8-hydroxyquinoline as a fluorometric reagent for gallium, and developed the fluorometric method for the determination of gallium in silicate rocks. Recently, J. W. Collat and B. Rogers[2] developed the simultaneous fluorometric spectrophotometric method with the modified spectoro-fluorometer.

The authors carried out the studies of the various conditions on the fluorometric procedure of gallium with 8-hydroxyquinoline.

REAGENT AND APPARATUS

Standard gallium solution, 10 μg Ga/ml ; Dissolve 0.100 g of pure gallium metal (impurity<15 p.p.m.) in hydrochloric acid and dilute to 100 ml. This stock solution was diluted with 0.1 *N* hydrochloric acid to prepare a solution of 10 μg Ga/ml as required. The solution should be 0.1 *N* in hydrochloric acid.

8-hydroxyquinoline solution, 1% ; Dissolve 1.0 g of purified 8-hydroxyquinoline in 6 ml of glacial acetic acid, and dilute to 100 ml.

Ammonium acetate solution, 20% ; dissolve 20 g of ammonium acetate in water, and dilute to 100ml.

1 *N* hydrochloric acid, C.P.

1 *N* ammonium hydroxide, C.P.

Fluorometric measurements were made with a fluorometer which was built in our laboratory[4]. pH measurements were made with the glass electrode pH meter (Shimadzu GU-1).

EXPERIMENTAL PESULTS

1. Fluorescence spectrum of Ga-oxinate and its stability

Ga-oxinate, $Ga(C_9H_6ON)_3$, was precipitated from acidic solution (pH 4.1),

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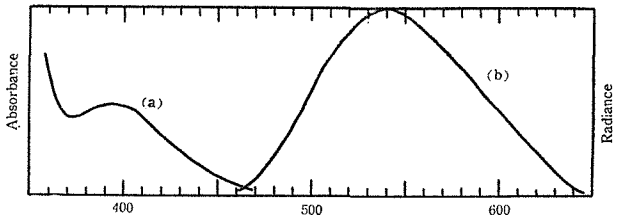
buffered with ammonium acetate and hydrochloric acid. The Ga-oxinate was dried at 110°C for 2~3 hours, then dissolved in proper amount of chloroform. This chloroform solution was irradiated with 365 mμ-Hg-line and the spectral distribution curve of Ga-oxinate was measured.

As seen in Fig. 1, Ga-oxinate had a fluorescence band from 450 to 650 mμ and the wavelength of its peak was about 540 mμ.

Fluorescence stability of Ga-oxinate, extracted into chloroform from the solution of pH 2.8 and 10.1, was measured and illustrated in Fig. 2. As seen in Fig. 2, the fluorescence intensity of Ga-oxinate was stable at least for 2 hours.



Wave Length (mμ)
(a) Absorption spectrum
(b) Luminescence spectrum

Fig. 1. Spectral distribution curves of Ga-oxinate.

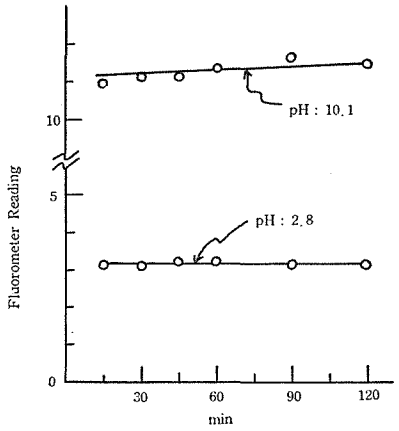


Fig. 2. Stability of Ga-oxinate.

2. Effect of pH

Effect of pH of solution on the fluorescence intensity in the extraction procedure was determined as follows.

0, 10 and 20 μg of gallium were taken respectively and added with 1 ml of 8-hydroxyquinoline solution and 5 ml of 20% ammonium acetate solution. Diluted to about 40 ml with water and added with sufficient amount of 1 *N* hydrochloric acid or 1*N* ammonium hydroxide to fall within a pH range of 1.8 to 10.1. And then the Ga-hydroxyquinoline complexes are extracted with 50 ml of chloroform and the fluorescence intensities of the chloroform solutions are

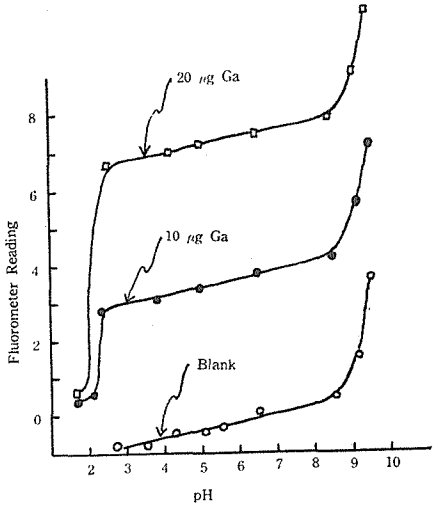


Fig. 3. Effect of pH.

measured. The results are shown in Fig. 3.

As seen in Fig. 3, the constant extraction rate of Ga-oxinate was obtained over the pH range from 2.8 to 10.1. The extracts from a basic medium show a intense fluorescence. It was considered that the fluorescence was due to excess 8-hydroxyquinoline reagent which fluoresced more intense at higher pH range. But in this region, the fluorescence intensity of the extracts was proportional to gallium contents. Accordingly fluorometric determination of gallium was performed by extraction at a definite pH value from 2.8 to 10.1.

3. Concentration of 8-Hydroxyquinoline

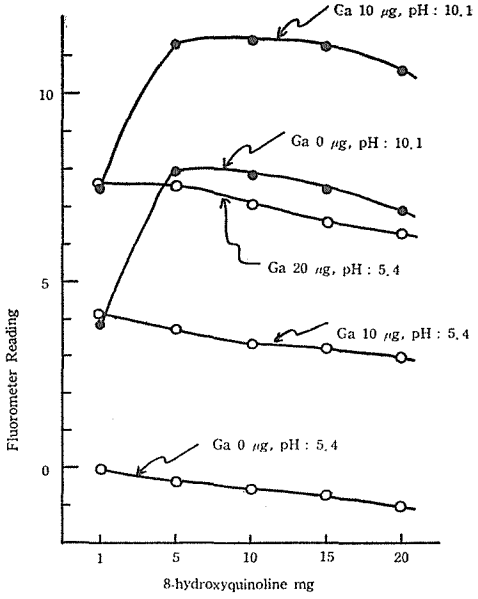


Fig. 4. Effect of amount of reagent.

Solution containing 0, 10 and 20 μg of gallium, varying amount of 8-hydroxyquinoline reagent and 5 ml of 20% ammonium acetate solution were extracted at a pH of 5.4 and 10.1 respectively, and its fluorescence intensity was measured. At the pH of 5.4 the intensity of fluorescence varied inversely with the amount of reagent added. On the other hand, at the pH of 10.1, the maximum fluorescence intensity was obtained by use of 5 mg oxine (1 ml of 5% 8-hydroxyquinoline 1 N acetic acid solution was used). With increasing the amount of 8-hydroxyquinoline reagent, the intensity of fluorescence decreased gradually. So as to obtain a good result that the amount of reagent is not deficient, was used 1 ml of 1% 8-hydroxyquinoline 1 N acetic acid solution. The results are shown in Fig. 4.

4. Determination of Gallium

According to the results described above, gallium may be quantified accurately by the following procedure :

Sample solutions containing 0~30 μg of gallium in a volume of approximately 40 ml are taken. Add 1 ml of 1% 8-hydroxyquinoline 1 N acetic acid solution, adjust to a definite pH of 2.8, 5.4, or 10.1, respectively. They are extracted three times with 10 ml portions of chloroform. The extracts are diluted to 50 ml with chloroform and drawn off through a small 9 cm dry filter paper, and the intensity of fluorescence was measured.

Fig. 5 shows the analytical curves obtained by the above mentioned procedure. In all cases the plot is linear up to 30 μg gallium per 50 ml. The

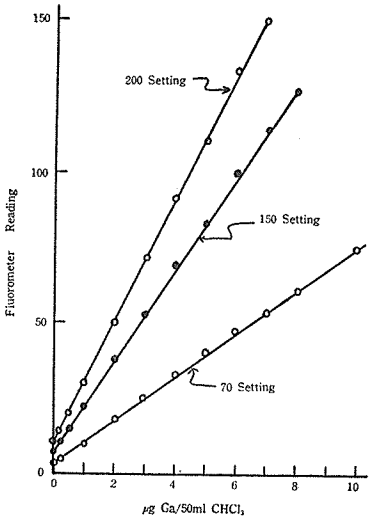


Fig. 5. Calibration curves.

sensitivity of this method was high and 2 μg of gallium per 50 ml chloroform was determined. The results of this experiments show that gallium can be determined in the range 2 to 30 μg per 50 ml chloroform with an average error of $\pm$ 0.4 μg.

Fig. 6 shows the analytical curves obtained by the same procedure, using

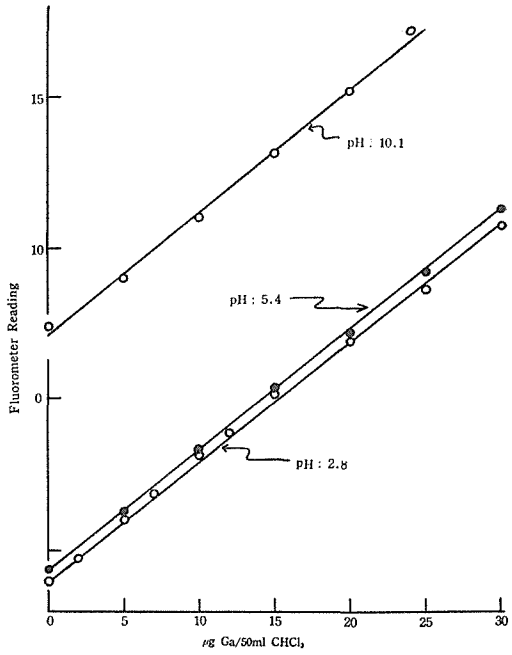


Fig. 6. Calibration curves.
Instrument was standardized against a solution of uranin, 0.16 μg per ml.

a Shimadzu universal fluorometer. In this case, the fluorometer was set at 70, 150 and 200 scale division using a standard uranium solution (0.16 μg uranin per ml aqueous solution).

5. Effect of Diverse Ions

Solutions containing 10 μg of gallium and definite quantities of various ions were taken and treated by the above mentioned procedure (at pH 2.8). The results are shown in Table 1.

When indium was present, its oxinate was extracted in chloroform from pH 2.8 solution and emitted fluorescence (Run. No. 7 and 8). Small amounts of indium less than 500 μg did not interfere at pH 2.6~2.7 as seen in Table 1 (Run. No. 3~5). A pH 2. 6, however, the fluorescence intensity of gallium oxinate was slightly weeker than that at pH 2.8 (approximately 5% lower results are obtained). At pH 2.6, 1 mg or more indium showed a fluorescence. As the positive result was obtained (Run, No. 6), large amounts of indium must have been absent.

Oxinates of ferric iron and vanadium were extracted by chloroform at pH 2.8 and interfered in the determination of gallium by its colour. In this case, these interfering actions could be prevented by the reduction with hydroxylamine hydrochloride. 500 μg ferric iron and 100 μg vanadate vanadium were easily reduced by adding 1 ml of 1% hydroxylamine hydrochloride solution and gallium was determined without interferences.

Copper, molybdate, citrate and tartrate interfered in this procedure. Large amounts of fluoride reduced the fluorescence of gallium.

Table 1. Effect of diverse ions.

Pun. No.	Diverse	Ions μg	Ga Found μg	Deviation μg
1	Al^{3+}	100	9.8	− 0.2
2		1000	9.9	− 0.1
3*	In^{3+}	50	9.9	− 0.1
4*		100	10.0	± 0
5*		500	9.1	− 0.9
6*		1000	11.9	+ 1.9
7		500	20.6	+10.6
8		100	18.2	+ 8.2
9	Tl^{3+}	500	9.4	− 0.6
10	Fe^{3+}	500	9.3	− 0.7
11	Y^{3+}	100	9.8	− 0.2
12	La^{3+}	500	9.7	− 0.3
13	Sm^{3+}	100	10.2	+ 0.2
14	Th^{4+}	200	9.9	− 0.1
15	Ge^{4+}	500	10.0	± 0
16	Cu^{2+}	100	5.4	− 4.6
17	Zn^{2+}	500	10.0	± 0
18	Cd^{2+}	500	10.0	± 0
19	Mg^{2+}	500	10.0	± 0
20	Be^{2+}	500	10.2	+ 0.2
21	Ca^{2+}	500	10.0	± 0
22	Ba^{2+}	500	10.2	+ 0.2
23	Ni^{2+}	500	10.0	± 0
24	Mn^{2+}	500	9.7	− 0.3
25	$Co^{2}{}_{+}$	500	9.5	− 0.5
26	UO_2^{2+}	500	10.0	± 0
27	MoO_4^{2-}	100	5.8	− 4.2
28	VO_3^-	100	9.4	− 0.6
29	F^-	100	9.1	− 0.9
30	PO_4^{3-}	500	9.8	− 0.2

* pH 2.6~2.7

DISCUSSION

As seen in Fig. 1, the gallium oxinate in chloroform showed the peak of absorption at 395 mμ and emitted the luminescence (luminescence band 450~650 : the peak 540 mμ). There was the mirror image relation between the absorption and the luminescence spectrum, *i. e.*

$$h\nu_a - h\nu_0 = h\nu_0 - h\nu_e$$

$$\nu_e = 2\nu_0 - \nu_a$$

where ν_a and ν_e are the oscillation numbers of the peaks on the absorption and excitation respectively, and $h\nu_0$ the difference between the lowest level of excitation and the ground state. h is Plank's constant. Then, the absorption of the gallium oxinate in chloroform at 395 mμ was comparatively stable, and the luminescence by 365 mμ Hg line excitation was also stable as shown in Fig. 2.

As the fluorescence was more distinct than its absorbance, the more trace amounts of gallium were measured by the fluorometric method than the colorimetric method.

The luminescence spectrum of gallium oxinate lies in longer wave length than that of aluminium oxinate, but nearly equal to that of indium oxinate and so one could not distingish these two elements.[3)]

The extraction procedure was performed at the comparatively low pH (*i. e.* at pH 2.8 or less), therefore, in the presence of Al, Co, Ni, Y, La *etc*, the corresponding oxinates were not extracted and the specific or selective determination of gallium was possible.

When indium was present, its luminescence band was similer to that of gallim oxinate, and indium oxinate was, more or less, extracted at pH 2.8. Therefore, it was desirable to extract the gallium oxinate at pH 2.6~2.7. Gallium was also determined with oxine according to the foregoing procedure at the pH value such as 5.4 or 10.1 respectively, as well as at pH 2.8. At such a high pH value, aluminium, indium and many other elements were also extracted and extremely interfered with the determination of gallium.

The fluorometric method of gallium developed in this paper was suitable for determining a trace amount of gallium such as 0.2~30 μg, being effective even when the gallium content was 0.004 μg/ml.

REFERENCES

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(4) M. Ishibashi, T. Shigematsu and Y. Nishikawa, *Japan Analyst*, **3**, 294 (1954).