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The Fluorometric Determination of Gallium in Aluminum Metal with 8-Quinolinethiol[1)]

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A method for the fluorometric determination of gallium in aluminum metal is presented which involves extraction with the methyl isobutyl ketone (MIBK) of the gallium 8-quinolinethiolate complex. The extracted complex has a greenish-yellow fluorescence, with an emission maximum at 505 nm. The maximum fluorescence intensity is obtained at a pH of the initial aqueous phase of around 3.3; the fluorescence remains stable for at least 2 hr. When 50 ml of a sample aqueous solution containing gallium and 0.2 ml of a 0.2% 8-quinolinethiol solution is subjected to extraction with 10 ml of MIBK, the quantity of gallium which can be present for determination in the sample solution amounts to 1 to 30 μg. For the removal of the interfering effects of zinc, cadmium, copper, and nickel on the fluorometric determination, gallium was extracted with isopropyl ether from a 7 M HCl solution. The relative error of this method was 5% for 0.019% gallium in aluminum metal.

The fluorometric determination of gallium with such reagents as oxine and rhodamine B has been proposed, and the application to gallium in aluminum metal has also been tested.[2,3)]

A benzene-extraction method for the fluorometric determination of gallium with 8-quinolinethiol was investigated by Korenman *et al.*[4)] and chloroform extraction, by Davis.[5)] However, in these studies no metal of any practical use was tested. Details on the analytical conditions are not available, and there exists disagreement between these studies as to the optimum conditions. 8-quinolinethiol does not react with aluminum and magnesium, but forms a stable complex with gallium. In view of these facts, the present authors examined the conditions in the determination of gallium in aluminum metal. MIBK was used as the extraction solvent.

Experimental

Reagents. Standard solution of gallium: A stock solution of gallium was prepared by dissolving 0.1819 g of 99.999% gallium metal (Mitsubishi Kinzoku Kogyo) in 6 M hydrochloric acid. The standard solution was prepared by diluting the stock solution. 0.2% 8-quinolinethiol solution: 0.1 g of 8-quinolinethiol hydrochloride (Dojin Yakka) was dissolved in 50 ml of 6 M hydrochloric acid.

10% L-ascorbic acid solution: 10 g of L-ascorbic acid was dissolved in water, and the mixture was diluted to 100 ml. This solution was freshly prepared for every experiment. 0.1% *O*-phenanthroline solution: 0.25 g of *O*-phenanthroline was dissolved in 10 ml of ethyl alcohol, and the mixture was diluted to 250 ml with water.

0.2 μg/ml uranine solution: 0.10 g of uranine was dissolved in water and diluted to 100 ml. The solution was then further diluted with water to make a solution containing 0.20 μg uranine per ml. The resultant solution was used as a reference standard to adjust the sensitivity of the fluorescence spectrophotometer.

Other reagents: The MIBK used as an extraction solvent and all the other chemicals were of an analytical grade. Under some conditions, ammonia was washed with an 8-quinolinethiol solution and MIBK.

Apparatus. The fluorometric measurements were carried out using a Hitachi fluorescence spectrophotometer, Model 203, with a mercury lamp. A 120 W Xenon lamp was used as the exciting source for the measurements of the fluorescence and excitation spectra. A 1 cm × 1 cm quartz cell was used. A Toa Denpa Model HM-5 A glass electrode pH meter was used for the pH measurements. An Iwaki KM shaker was used.

Procedure. A sample solution containing less than about 10 μg of gallium was transferred into a beaker. Then, 0.2 ml of the 0.2% 8-quinolinethiol solution and 5 ml of the 10% ascorbic acid solution were added to the solution. After the solution has been diluted to 50 ml with water, the pH of the solution was adjusted to 3.3 with dilute hydrochloric acid or ammonia. The resultant aqueous solution was then transferred into a separatory funnel. The gallium complex was extracted for 5 min with 10 ml of MIBK. After the separation of the aqueous phase, the fluorescence intensity of the organic phase was measured using a uranine solution as a reference standard. The amount of gallium was evaluated from the calibration curve. The excitation and fluorescence wavelengths used were 365 and 505 nm (exciting source: a mercury lamp) respectively.

Results and Discussion

Excitation and Fluorescence Spectra. 8-Quinolinethiol reacts with gallium to form a complex of a yellowish-green fluorescence. The complex showed an excitation maximum at 395 nm and a fluorescence maximum at

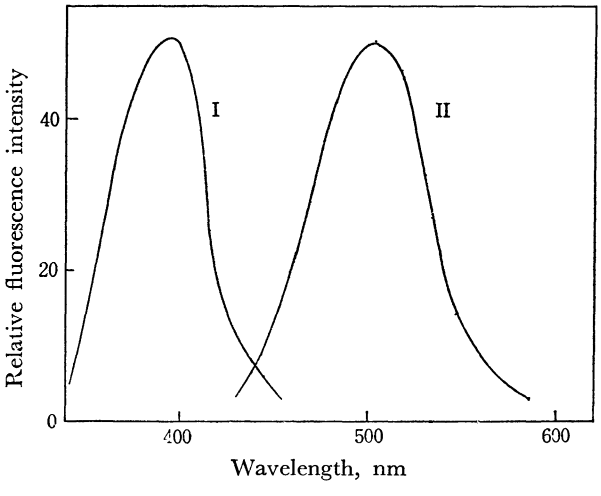

Fig. 1. Excitation and fluorescence spectra.
Excitation spectrum(I): Excited with xenon lamp and analyzed at wavelength for maximum fluorescence intensity.
Emission spectrum(II): Excited at 395 nm.

505 nm (exciting source: Xenon lamp). The apparent spectra are shown in Fig. 1.

Effect of the Amount of 8-quinolinethiol. The effect of the concentration of 8-quinolinethiol was investigated by adding various amounts of the reagent to a solution containing 5.8 μg of gallium. As is shown in Fig. 2, the maximum fluorescence intensity was obtained by the use of 0.1—0.2 ml of the 0.2% 8-quinolinethiol solution; above 0.2 ml of 8-quinolinethiol the fluorescence intensity decreased gradually in direct proportion to the amount of the reagent added. The fluorescence intensity of the reagent blank was found to be constant.

Effect of pH. The effect of the pH of the aqueous phase on the extraction was also studied. The results are shown in Fig. 3. The fluorescence intensity showed a maximum at pH 3.2—3.4. When the pH was higher than 3.5, the intensity decreased and became negligibly low at pH 11. Therefore, all the extractions were carried out at pH 3.3. According to Korenman, the optimum pH in a benzene extraction was 5, but Davis found that it was 3. The present result is in agreement with that of Davis.

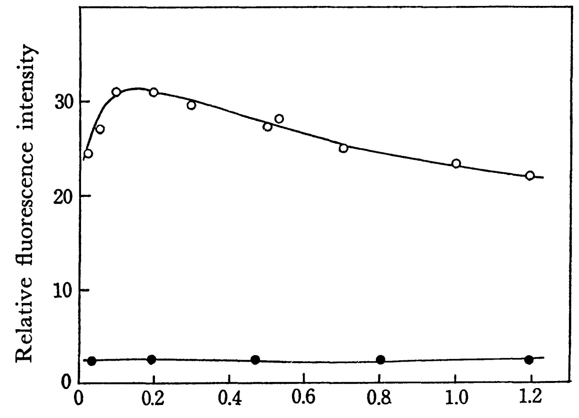

Fig. 2. Effect of amount of reagent.
—○— Ga: 5.8 μg pH: 3.5
—●— Reagent blank

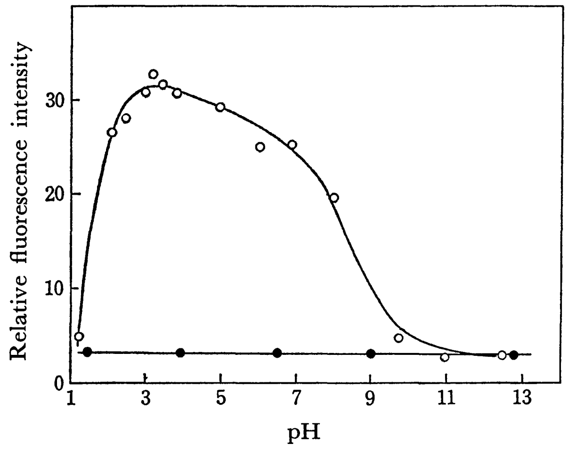

Fig. 3. Effect of pH on fluorescence intensity.
—○— Ga: 5.8 μg 0.2% 8-quinolinethiol: 0.2 ml
—●— Reagent blank

The pH was adjusted by adding hydrochloric acid or ammonia. The buffer solution used was a L-ascorbic acid solution. As the old ascorbic acid solution reduced the fluorescence intensity of the gallium complex, the solution was freshly prepared for each experiment.

Effect of the Shaking Time. The effect of the shaking time was tested in the range from 0.5 to 10 min. It was found that a 3-min shaking was sufficient. 5 min was chosen for shaking in the present experiments, though. The fluorescence intensity of an extracted complex was stable for at least 2 hr at room temperature.

Effect of the Volume of Aqueous Solution. When MIBK was used for the extraction of the chelate in water, a small amount of MIBK dissolved in the aqueous layer. For the investigation of the effect of the aqueous solution, the volume of the organic phase of MIBK was kept at 10 ml, while that of the aqueous phase was varied from 40 ml to 140 ml. As is shown in Fig. 4, the fluorescence intensity gradually increased in proportion to the volume of the aqueous phase, although no great effect of the volume of the aqueous solution on the intensity was observed.

Effect of Foreign Ions. The effect of 25 kinds of ions coexistent with 5.8 μg gallium was studied. The results are summarized in Table 1. The following ions did not interfere: aluminum, magnesium, calcium, chromium, scandium, lanthanum, titanium, zirconium, manganese, barium, and strontium ions. Zinc ions gave a positive error. A small amount of cobalt, nickel, copper, bismuth, iron, and silver ions reduced the fluorescence intensity. One milligram of vanadium ions (VO_3^-) reduced by ascorbic acid did not interfere. To remove some interfering ions in the above ions contained in aluminum metals, an isopropyl ether extraction method[6] was used.

The gallium chloride complex is extracted from the 7 M hydrochloric acid solution with isopropyl ether; then the organic phase is washed with 7 M hydrochloric acid, so that some interfering ions are completely removed from the gallium in the organic layer. In this separating method, zinc (up to 5 mg), cadmium (1.7 mg), copper (5 mg), nickel (1 mg), and cobalt (1 mg) do not interfere. Iron (III) is reduced to iron (II), masked with *O*-phenanthroline. However, the

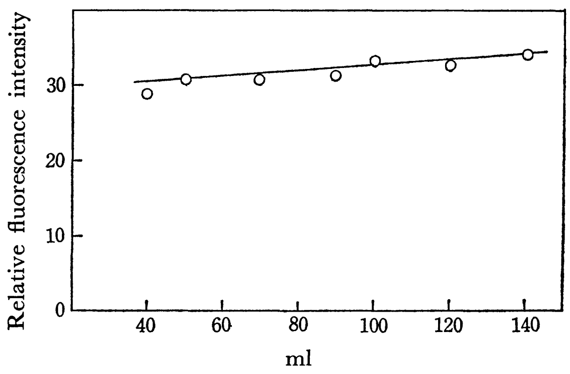

Fig. 4. Effect of volume of aqueous solution.
Ga: 5.8 μg 0.2% 8-quinolinethiol: 0.2 ml
pH: 3.5

TABLE 1. EFFECT OF FOREIGN IONS

Ions	(mg)	Added as	Ga found (μg)
Al^{3+}	10.0	$Al(NO_3)_3 \cdot 9H_2O$	5.8
	250.0	$Al(NO_3)_3 \cdot 9H_2O$	5.8
Ca^{2+}	2.0	$Ca(NO_3)_2$	5.8
Mg^{2+}	200.0	$MgSO_4$	5.8
Cr^{3+}	1.0	$Cr(NO_3)_3 \cdot 9H_2O$	5.8
Mn^{2+}	1.0	$MnSO_4$	5.8
La^{3+}	1.5	$La_2O_3 + HCl$	5.8
Sc^{3+}	1.0	$Sc_2O_3 + HCl$	5.8
Pb^{2+}	0.1	$Pb(NO_3)_2 \cdot H_2O$	5.8
Bi^{3+}	0.1	$Bi(NO_3)_3 \cdot 5H_2O$	3.3
Ba^{2+}	1.0	$BaCl_2 \cdot 2H_2O$	5.8
Sr^{2+}	1.0	$Sr(NO_3)_2$	5.7
ZrO^{2+}	1.0	$ZrOCl_2 \cdot 8H_2O$	5.4
Tl^{+}	0.1	$TlNO_3$	5.2
Ag^{+}	0.1	$AgNO_3$	0.2
Cu^{2+}	0.008	$CuSO_4 \cdot 5H_2O$	5.5
	0.02	$CuSO_4 \cdot 5H_2O$	4.8
Fe^{3+}	0.02	$NH_4Fe(SO_4)_2 \cdot 12H_2O$	5.4
	0.1	$NH_4Fe(SO_4)_2 \cdot 12H_2O$ + 5% ascorbic acid 5 ml	5.6
Ni^{2+}	0.02	$NiSO_4 \cdot 6H_2O$	3.2
Zn^{2+}	0.006	$Zn + HCl$	8.5
Ti^{4+}	0.1	$Ti(SO_4)_2$	5.8
VO_3^{-}	1.0	NH_4VO_3	1.3
	1.0	NH_4VO_3 + 5% ascorbic acid 5 ml	5.8
Hg^{2+}	0.1	$HgCl_2$	4.4
Co^{2+}	0.02	$Co(NO_3)_2 \cdot 6H_2O$	3.4
Sn^{2+}	0.04	$SnCl_2 \cdot 2H_2O$	5.8
In^{3+}	0.015	$In + HCl$	5.7
Sb^{3+}	0.1	$SbCl_3$	5.9

Ga taken: 5.8 g; 0.2% 8-quinolinethiol: 0.2 ml; pH: 3.3

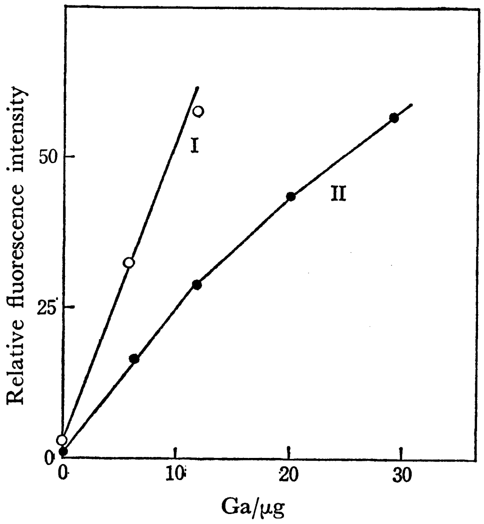

Fig. 5. Calibration curves for gallium.
Fluorometer reading was set at 50 div. (curve I) or 25 div. (curve II) with the uranine reference solution (0.2 μg uranine/ml)

TABLE 2. ANALYTICAL RESULTS FOR SYNTHETIC SAMPLES

Sample No.	Ga taken (μg)	Foreign ions (mg)	Ga found (μg)
1	3.2	$\{Al^{3+}$ 50, Mg^{2+} 10, Mn^{2+} 1, Fe^{3+} 0.5, VO_3^{-} 0.1$\}$	3.3, 3.4, 3.4
2	6.3	(Al^{3+} 60, Zn^{2+} 5)	6.5, 6.2, 6.4
3	0.0	(Zn^{2+} 2.5, Cd^{2+} 1.7)	0.0, 0.0, 0.1
4	3.2 6.3	$\{Cu^{2+}$ 5, Ni^{2+} 1, Co^{2+} 1, Mn^{2+} 1, Fe^{3+} 0.1$\}$	3.5, 3.2, 3.3 6.4, 6.5, 6.5
5	3.2 6.3	$\{Al^{3+}$ 30, Mg^{2+} 10, Zn^{2+} 2.5 Cu^{2+} 2, Cr^{3+} 1, SiO_3^{2-} 1$\}$	3.0, 3.2, 3.4 6.5, 6.5, 6.3

iron *O*-phenanthroline complex increases the blank value slightly; therefore, a large amount of iron ions interferes.

Calibration Curves. The calibration curves for the determination of gallium were prepared under optimum conditions. The results are shown in Fig. 5. The I calibration curve was obtained by setting up the fluorometer at 50 using the standard uranine solution. The II curve was set at 25.

A linear relationship between the fluorescence intensity and the concentration of gallium was obtained over the concentration range of 0—10 μg of gallium per 10 ml of MIBK. The possible range for the accurate determination of gallium was 1—30 μg.

Synthetic Samples. The determination of gallium in some synthetic samples was done. For a synthetic sample containing copper, cobalt, nickel, and iron, which interfere significantly when present in even small amounts, both the gallium and the iron (III) were extracted with isopropyl ether from a 7 M hydrochloric acid solution. Then the iron (III) was reduced by an ascorbic acid solution, masked with *O*-phenanthroline. Table 2—4 shows the results of the determination of gallium. The samples containing zinc were treated in the same way as above (Tables 2-2, 3, 5). For a sample containing aluminum, magnesium, iron, and vanadium, the ether extraction was omitted and the gallium 8-quinolinethiolate was directly extracted with MIBK. The results are shown in Table 2-1.

In all of the cases studied in these synthetic samples, the gallium could be determined with an average error of 3 percent.

Determination of Gallium in Aluminum Metal. From the experimental results described above, a recommendable procedure is as follows: Dissolve 0.1—0.3 g of a sample in 50 ml of hot 7 M hydrochloric acid. Transfer the resultant solution to a 100-ml volumetric flask. Bring up to the mark with a 7 M hydrochloric acid solution. Pipet a 10 ml aliquot into a 100-ml beaker, and add 20 ml of 7 M hydrochloric acid. Transfer the solution to a separatory funnel and shake for 5 min with 20 ml of isopropyl ether. After this extraction has been repeated twice using 10 ml of isopropyl ether, discard the aqueous phase. Wash the resultant ether solution two times, with 20-ml and 10-ml portions of 7 M hydrochloric acid. Then add 20 ml of water to the ether phase. Evaporate only the ether phase on a sand bath, and then cool the water phase. Add 5 ml of 5% ascorbic acid solution and 2 ml of a 0.1% *O*-phenanthroline solution to the

TABLE 3. ANALYTICAL RESULTS FOR STANDARD SAMPLE NBS 85 B

Amount of sample taken 2.651 mg/ml	Present method		2-Methyl-8-quinolinol method[3,7]	
	Ga found (μg)	Ga %	Ga found (μg)	Ga %
10 ml	5.3	0.020	5.1	0.019
	5.1	0.019	5.3	0.020
	5.3	0.020	5.2	0.020
20 ml	11.2	0.021		
	10.9	0.021		

Relative error: 5% for 0.019% gallium (standard sample NBS 85 B).

aqueous solution remaining in the beaker. After the dilution of the solution to 50 ml, add 0.2 ml of 0.2% 8-quinolinethiol and adjust the pH of the solution to 3.3. Transfer the solution to a separatory funnel, and then extract the gallium 8-quinolinethiolate complex by shaking for 5 min with 10 ml of MIBK. Then filter out the organic phase through a cotton plug. Transfer the extract to a quartz cell. The fluorescence intensity at 505 nm is measured at an excitation wavelength of 365 nm with reference to a 0.2 μg/ml uranine solution.

The accuracies of the amount of gallium in a sample as determined by the present method and by the conventional 2-methyl-8-quinolinol method[3,7] are shown in Table 3. The present method is shown to be accurate enough for the determination of gallium in the aluminum metal.

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