A New Spectrophotometric Determination of Gallium with Capri Blue*

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It is well known that, when gallium is spectrophotometrically determined with acid dyes, the chlorogallate ion $[GaCl_4]^-$ produced in strong hydrochloric acid media (ca. 6 N) reacts with acid dyes to produce chelates, which are then extracted with organic solvents.1) In previous papers,2,3) triphenylmethaneamino derivative dyes were used to determine some metal ions. Jankovský4) and other workers5) reported that gallium is determined spectrophotometrically with the following two dyes; Malachite green and Brilliant green. We considered, however, that the dyes employed by them were probably unsuitable for this determination because of the small values of their apparent dissociation constants.

Capri blue (3-diethylamino-7-dimethylamino-2-methyl phenazoxonium chloride) is stable in a strong hydrochloric acid solution because its apparent dissociation constant is large.6) However, it has not yet been applied to the determination of metal ions.

In this paper, a new method is described for the spectrophotometric determination of small amounts of gallium. It is based on the formation of a colored complex of gallium with Capril blue in a hydrochloric acid solution. The complex is extracted with benzene.

Experimental

Reagents.—*Gallium Stock Solution.*—About 3 g. of gallium nitrate crystal ($Ga(NO_3)\cdot 8H_2O$ Mitsuwa Yakuhin Co.) was dissolved in 100 ml. of 6 N hydrochloric acid and titrated with an EDTA standard solution, using Cu-PAN7) as an indicator. The working solution containing 1 μg./ml. was prepared from this solution by successive dilution with 6 N hydrochloric acid.

Capri Blue.—Two grams of commercial Capri blue (Tokyo Kasei Co.) was dissolved in 100 ml. of 6 N hydrochloric acid.

Benzene.—Commercial benzene was purified in the usual manner.

Apparatus.—The spectrophotometric absorbances were measured with a Shimadzu spectrophotometer Model QB-50 and a Hitachi photometer Model EPW-4, with 1 cm. cells.

Procedure.—Transfer the sample solution (less than 20 μg. Ga) in 6 N hydrochloric acid to a separate funnel and add 3 ml. of 2% Capri blue in a 6 N hydrochloric acid solution. Shake the solution for 1 min. with 20 ml. of benzene. Make up the benzene layer to 25 ml. with benzene. Centrifuge for 1 min. and measure the absorbance at 655 mμ (Filter 66) with the reagent blank solution as a reference. Determine the amount of gallium in the sample from a calibration curve prepared similarly.

Results

The Effect of the Acidity of Hydrochloric Acid and the Absorption Spectra.—The absorbance of the sample solution was measured in the 500—680 mμ range, using the reagent as a

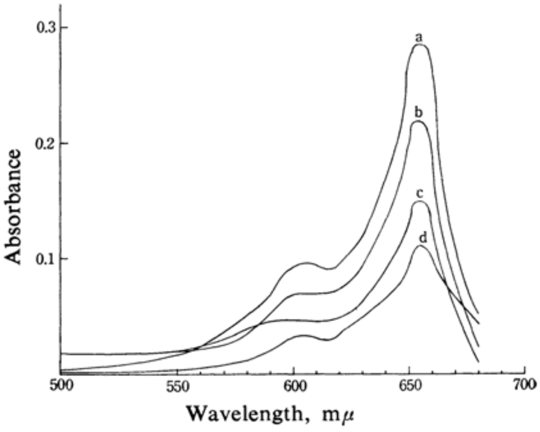

Fig. 1. Absorption spectra of Capril blue and its gallium complex benzene solution.
Ga 10^{-4} M, 3 ml.+Dye soln. 2%, 3 ml./25 ml.
Benzene, 25 ml.
a: 6 N HCl vs. reagent blank
b: 4 N HCl vs. reagent blank
c: 8 N HCl vs. reagent blank
d: Reagent blank vs. benzene.

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TABLE I. MOLAR EXTINCTION COEFFICIENTS OF VARIOUS DYES

Dye	Gallium		Absorbance	Measured wavelength mμ	Molar extinction coefficient
	Concn. mol.	Added ml.			
Capri blue	5×10^{-5}	2	0.226	655	5.6×10^4
Rhodamine b*(1)	1×10^{-4}	3	0.385	570	3.2×10^4
Malachite green*(4)	1×10^{-4}	5	0.580	635	2.9×10^4
Brilliant green*(5)	1×10^{-4}	5	0.300	640	1.5×10^4

* Data was obtained by ref. described procedure.

TABLE II. EFFECT OF AMOUNT OF DYE SOLUTION ADDED

Gallium 5×10^{-5} M ml.	Capri blue		Absorbance	Blank value
	Concn. %	Added ml.		
2.0	2.0	2.0	0.219	0.080
2.0	2.0	3.0	0.227	0.098
2.0	2.0	4.0	0.228	0.101

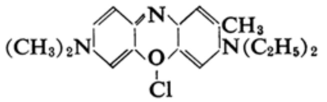

TABLE III. STABILITY OF GALLIUM-CAPRI BLUE COLORED BENZENE SOLUTION

Standing time, min.	0	30	60	90	120
Absorbance	0.226	0.226	0.226	0.226	0.226

Gallium taken: 2 ml. (5×10^{-5} M); Dye soln.: 2%, 3 ml.

reference. The extractability of a gallium-Capri blue complex, with benzene as a function of hydrochloric acid, is shown in Fig. 1. The maximum absorbance of the complex is at about 655 mμ. The absorbance of the sample solution is the greatest, and the absorbance of the blank solution is the smallest, when the complex is extracted from a 6 N hydrochloric acid solution.

The molar extinction coefficient of the gallium-Capri blue complex in benzene is about 5.6×10^4 at 655 mμ. The molar extinction coefficients of various complexes used for the colorimetric determination of gallium are compared in Table I; the Capri blue complex is very sensitive.

The Effect of the Amount of the Dye and the Stability of the Colored Complex. — The amount of Capri blue solution added was varied, the other factors remaining unchanged. The results are shown in Table II. The absorbance is constant on the addition of more than 3 ml. of a 2% Capri blue solution. When too much is added, however, the absorbance of the reference increases. The stability of the colored complex in a benzene solution was investigated as shown in Table III. The complex is stable in benzene for 2 hr.

Calibration Curve.—Various amounts of a standard gallium solution containing more than 1 μg. of gallium were used in the manner

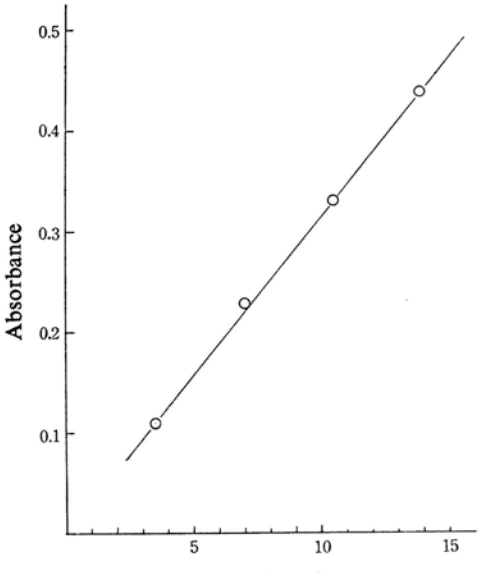

Fig. 2. Calibration curve.
Dye soln.: 2%, 3 ml., measured at 655 mμ

described above. The relationship between the absorbance and the amount of gallium obeys Beer's law for 1—15 μg. of gallium as is shown in Fig. 2.

The Effect of Foreign Ions.—The effect of foreign ions was studied with a solution containing 2 ml. of 5×10^{-5} mol. (8.7 μg.) of gallium and various ions. Alkali metal salts of the anions were used. Cations were added as chloride or nitrate.

Under these conditions no interference was observed from about fifty-fold (0.5 mg.) amounts of aluminum, antimony, calcium, cadmium, cobaltous, cupric, magnesium, manganese, indium or thallium ions. However, even a minute quantity of iron (both II and III) interferes seriously. Five millimicrograms of iron, for instance, doubled the apparent gallium content. Of the few anions examined, large excesses (1 mg.) of nitrate and sulafte were without effect.

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