The Spectrophotometric Determination of Gallium(III) with Xylenol Orange[1]

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The color reaction between gallium(III) and xylenol orange [bis-di(carboxymethyl)-aminomethyl-*o*-cresolsulfonephthalein] was first studied by Přibil and Kopanica,[2] who used the reagent for the detection of traces of gallium in the presence of ammonium fluoride and triethanolamine, which served as masking agents for other metal cations. The quantitative determination of gallium based on this reaction has not yet, however, been reported by any workers. It has only been disclosed that, depending on the pH value of the solution, gallium(III) reacts with xylenol orange to form two complexes, with metal-ligand ratios of 1 to 1 and 1 to 2. These reactions are applicable to the spectrophotometric determination of up to 60 μg. of gallium in 25 ml.

Experimental

Reagents.—*Standard Gallium Solution.*—A standard gallium(III) solution was prepared by dissolving 0.6980 g. of pure gallium metal (99.999% pure) in dilute sulfuric acid and then diluting it with water to 1 l. The concentration of sulfuric acid in this solution was about 0.05 M. Working solutions of gallium were prepared by diluting the standard solution with water.

Xylenol Orange Solution.—A 1×10^{-3} M xylenol orange solution was prepared by dissolving the Dotite XO reagent (disodium salt), which was used without further purification, in distilled water.

Nitric acid or a mixture of 0.5 M acetic acid and a 0.5 M sodium acetate solution was used for the regulation of the pH value. The former was used for pH values below 2, and the latter for pH values above 2.5. Solutions of diverse ions were prepared by dissolving the respective compounds (all reagent-grade chemicals) in distilled water in appropriate concentrations.

Apparatus.—A Hitachi spectrophotometer, model EPV-2, was employed, with 1 cm. cells, for all the absorbance measurements. A Shimadzu glass-electrode pH meter, model GU-1, was employed for all the pH determinations.

The Standard Procedure for the Determination.—To a sample solution containing gallium in a 50-ml. Erlenmeyer flask, a desired amount of nitric acid or 5 ml. of the acetate buffer, a given amount of the xylenol orange solution and a small amount of water were added to make the solution about 20 ml. when the sample solution contained aluminum(III), thorium(IV) or zirconium(IV), about 60 μmol. of potassium fluoride was added before the addition of the xylenol orange solution. The solution was heated in a boiling water bath for a few minutes, cooled with running water, transferred

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[1] This work was presented in part at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

[2] R. Přibil and M. Kopanica, *Microchim. Acta*, **1962**, 29; *Chem. Abstr.*, **56**, 13530 (1962).

to a 25 ml. volumetric flask and diluted with water to the mark. The resulting solution was kept for about 30 min. in a thermostat at 25 ± 0.5°C. The absorbance of the solution was then measured at the given wavelengths.

Results and Discussion

Absorption Curves.—The visual absorption curves of the gallium - xylenol orange mixture at different pH values are shown in Figs. 1 and 2. These curves were obtained by measuring the absorbance of the colored solutions containing 34.9 μg. of gallium against a reagent blank containing the same amount of xylenol orange. Between pH 0.9 and 1.4, the solutions give identical absorption curves, with one absorption maximum at 530 mμ. Above pH 2, the position of the maximum absorption shifts toward shorter wavelengths with an increase in the pH value. The curves obtained at pH 2.0 and 2.5 have a shoulder at about 545 mμ. Between pH 3.0 and 5.5, however, the solutions again give identical absorption curves, with one absorption maximum at 502 mμ. The slight blue shift in the position of the absorption maximum which was observed at pH 6.1 seems to be caused by the contribution of the absorption by the reagent blank, which absorbs strongly in the wavelength range from 510 to 600 mμ and which decreases its absorbance at shorter wavelengths over pH 6.0. Therefore, it may be concluded that, in the presence of an excess of xylenol orange, two complexes are formed between gallium and xylenol orange.

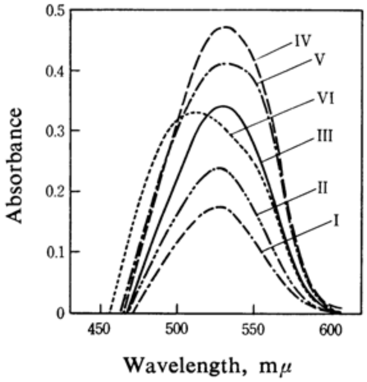

Fig. 1. Absorption curves of Ga-XO in the pH value range from 0.9 to 2.5.
Ga: 2.0×10^{-5} M (34.9 μg.), XO: 1.57×10^{-4} M
Reference: a reagent blank, pH: I, 0.9; II, 1.0; III, 1.1; IV, 1.4; V, 2.0; VI, 2.5

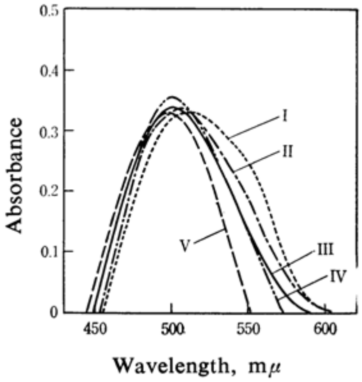

Fig. 2. Absorption curves of Ga-XO in the pH value range from 2.5 to 6.1.
Ga: 2.0×10^{-5} M (34.9 μg.), XO: 1.56×10^{-4} M
Reference: a reagent blank
pH: I, 2.5; II, 3.0; III, 4.5; IV, 5.0—5.5; V, 6.1

The Effect of pH.—The effect of pH on the absorbance of the solution was examined by measuring, at two wavelengths, 530 and 502 mμ, the absorbance of a solution containing 34.9 μg. of gallium and 4 ml. of a 1×10^{-3} M solution of xylenol orange. From the curves shown in Fig. 3, it was found that the maximum absorbance is obtained in the pH value range from 1.2 to 1.7 when measured at 530 mμ and from 4.5 to 5.5 when measured at 502 mμ.

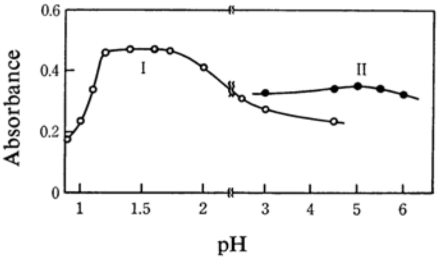

Fig. 3. Effect of pH on absorbance of the complexes at their absorption maxima.
Ga: 34.9 μg., XO: 1.57×10^{-4} M
Reference: a reagent blank
I: at 530 mμ, II: at 502 mμ

The Effect of the Amount of Xylenol Orange.—The effect of the reagent concentration was studied with solutions containing a given amount of gallium and varying amounts of a

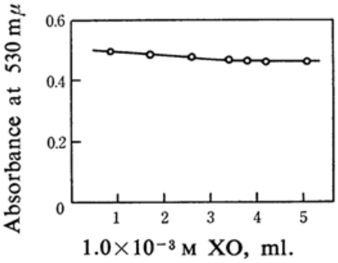

Fig. 4. Effect of amount of XO.
Ga: 34.9 μg., pH: 1.5
Reference: a reagent blank

1×10^{-3} M solution of xylenol orange. The pH values of the solutions were kept constant at 1.5, and the absorbance measurements were carried out at 530 mμ. The results are shown in Fig. 4. A constant absorbance is obtained when 3.5 to 5 ml. of the reagent solution is used. Therefore, 4 ml. of the reagent solution was used in further experiments.

The Stability of the Color.—The color formation does not occur instantaneously at room temperature. However, it is greatly accerelated by heating; the maximum color development is attained within only a few minutes when the mixture is heated in a boiling water bath. The absorbance remains almost constant for at least 6 hr. after preparation at pH 1.5 and for about 1.5 hr. when prepared at pH 5.5.

Calibration Curves for the Gallium Determination.—The calibration curves for the gallium determination were prepared in the manner described above with solutions containing no fluoride or 60 μmol. of fluoride. In all three curves shown in Fig. 5, linear relationships between absorbance and concentration are found to hold up to 60 μg. of gallium in 25 ml.

The apparent molar extinction coefficients of the two complexes, which were calculated from curves I and III, were found to be 22900 and 16300 respectively. According to Sandell's notation,[3] the sensitivities of the reactions are 0.003 μg. of gallium per cm² at 530 mμ and 0.004 μg. of gallium per cm² at 502 mμ.

The Effect of Diverse Ions.—The effect of diverse ions on the determination of gallium was then examined with the complex formed at pH 1.5, and the tolerance limit was calculated in each case. The tolerance limit was tentatively defined as the concentration of the foreign ion which affects the absorbance of the system by less than ± 3%. The results are summarized in Table I, from which it may be seen that bismuth(III), iron(III), thorium(IV) and ethylenediaminetetraacetic acid(EDTA)

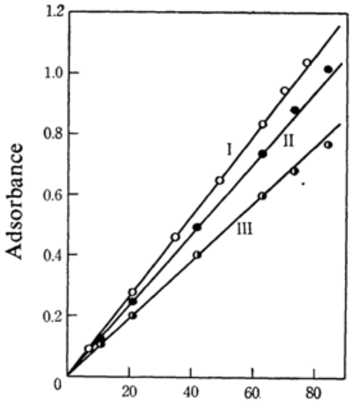

Fig. 5. Calibration curves.

I: in the absence of fluoride; pH: 1.5, 530 mμ
II: in the presence of 60 μmol. of fluoride; pH: 1.5; 530 mμ
III: pH: 5.5; 502 mμ

TABLE I. EFFECT OF DIVERSE IONS
Ga taken: 34.9 μg.

Diverse ion	μmol.	Relative error %	Tolerance limit μmol.
Al(III)	0.5 0.5*	+ 5.7 − 1.2	0.25 1.2
Bi(III)	0.5	+90.4	0
Cd(II)	0.5	− 0.4	large excess
Ce(III)	0.5	± 0.0	large excess
Co(II)	0.5	+ 0.4	large excess
Cr(III)	0.5	+ 0.9	1.1
Cu(II)	0.5	+ 1.8	0.8
Fe(III)	0.5 1.0**	+20.6 − 0.5	0.08 large excess
Hg(II)	0.5	− 0.2	large excess
Mn(II)	0.5	± 0.0	large excess
Ni(II)	0.5	± 0.4	large excess
Pb(II)	0.5	+ 0.7	2.1
Pd(II)	0.5 1.0**	+ 3.1 − 1.0	0.5 large excess
Th(IV)	0.5 0.5* 1.0*	+77.6 + 0.2 +37.7	0
Ti(IV)	0.5	+ 1.3	1.2
Tl(III)	2.0**	− 0.2	large excess
U(VI)	0.5	+ 0.4	large excess
V(IV)	0.5 2.0***	+ 4.6 − 0.5	0.3 large excess
Zn(II)	0.5	± 0.0	large excess
Zr(IV)	0.5 0.5*	+11.0 + 5.6	0.1 0.3
F^-	10 25 100	− 2.9 − 5.7 −19.3	10
Cl^-	500	− 0.2	large excess
$SO_2{}^{4-}$	500	− 7.2	200
$C_2O_2{}^{4-}$	0.5 2.0	−12.9 −36.4	0.1
$C_4H_4O_2{}^{6-}$	50 100	− 1.8 − 3.5	90
$C_6H_5O_3{}^{7-}$	5 20	− 0.2 − 0.4	>20
$PO_3{}^{4-}$	20 100	− 1.5 − 5.0	60
NTA	0.2 0.5	−27.6 −56.8	0
EDTA	0.1 0.2	−20.0 −37.3	0

* 60 μmol. of F^- added.
** 60 μmol. of F^- and 1 ml. of 5% ascorbic acid added.
*** 60 μmol. of F^- and 2 drops of 3% H_2O_2 added.

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3) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 2nd Ed., Interscience Publishers, New York (1950), p. 49.

interfere in even the smallest concentrations examined, but that some interfering cations, including aluminum(III), thorium(IV) and zirconium(IV), are partly masked by adding 60 μmol. of potassium fluoride. The interference of iron(III), palladium(II) and thallium(III) can be eliminated by the addition of such a reducing agent as ascorbic acid or sodium sulfite.

Comparison with Other Methods.—Some sensitive reagents, including rhodamine B,[4] 5,7-dichloro-8-oxine,[5] 2-(2-hydroxy-3-chloro-5-nitrophenylazo)-1-hydroxy-8-aminonaphthalene-3,6-disulfonic acid,[6] rhodamine 6G,[7] 3,4-dihydroxybenzene-4-arsonic acid (stilbazo),[8] 2,2′,4′-trihydroxy-5-chloroazobenzene-3-sulfonic acid (luminogallion IREA),[9] quercetin[10] and 1-(2-pyridylazo)-2-naphthol[11] (PAN) have been used for the determination of gallium. These reagents, except stilbazo and PAN, have been used as spectrofluorometric reagents for gallium. Of the reagents which react with gallium to form water-soluble complexes, stilbazo is found to be the most sensitive to gallium. The present method using xylenol orange is very sensitive and is comparable with the stilbazo or the luminogallion IREA method in sensitivity.

The Compositions of the Complexes.—The compositions of the two complexes were determined by the following two methods. The method developed by Frank and Oswalt[12] and by Furman and Garner[13] was employed for determining the composition of the complex with an absorption maximum at 530 mμ, and the competing equilibrium method was employed for determining that with an absorption maximum at 502 mμ.

The Complex with Its Absorption Maximum at 530 mμ.—An attempt to discover the composition was made with solutions with a given molar concentration of gallium at a given pH value, but with varying xylenol orange concentrations. If only a 1 to 1 complex is formed under certain conditions, and the absorbance, D, is measured against a reagent blank, the following relationship may be derived:

$$ab/D=(a+b)/(\varepsilon_{\mathrm{C}}-\varepsilon_{\mathrm{XO}})+1/K'_1(\varepsilon_{\mathrm{C}}-\varepsilon_{\mathrm{XO}}) \qquad (1)$$

where a and b represent the total molar concentrations of gallium and xylenol orang respectively; $\varepsilon_{\mathrm{XO}}$ and ε_{C}, the molar extinction coefficients of xylenol orange and the complex respectively, and K'_1, the apparent formation constant of the complex at the given pH value.

In Fig. 6 ab/D is plotted against $(a+b)$ at five wavelengths between 500 and 540 mμ. In these solutions, the concentration of gallium was 2.0×10^{-5} M, while the concentration of xylenol orange varied from 0.8×10^{-4} to 8×10^{-4} M; the pH value of these solutions was held constant at 1.0. The very good linearity of the curves in Fig. 6 supports the assumptions inherent in Eq. 1, indicating that only a 1 to 1 complex is formed under the conditions investigated.

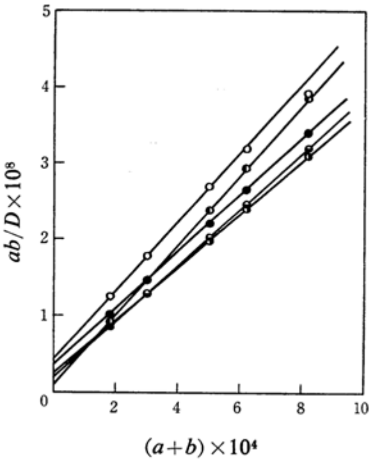

Fig. 6. Plots of ab/D vs. $(a+q)$ at various wavelengths.
—○—: 500 mμ, —●—: 510 mμ,
—◑—: 520 mμ, —◒—: 530 mμ,
—◐—: 540 mu, pH: 1.0

The Complex with Its Absorption Maximum at 502 mμ.—A substitution reaction between the complex and EDTA was used to ascertain the result obtained by the mole ratio method, which showed the presence of a 1 to 2 complex in the metal-ligand ratio. This is based on the fact that, at pH 5.5, EDTA can form a far more stable complex with gallium than does xylenol orange, and that, therefore, the xylenol orange in the gallium complex may be replaced by EDTA. A preliminary test showed that nitrilotriacetic acid (NTA) can also form a stable complex with gallium in a slightly acid medium, but it cannot extinguish the color of the gallium-xylenol orange complex at all. Therefore, it may be assumed that, in the presence of an excess of xylenol orange, the

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[4] H. Onishi, *Anal. Chem.*, **27**, 832 (1955).

[5] A. P. Golovina and I. P. Alimarin, *Vestnik Moskov. Univ.* **12**, *Ser. Mat. Mekh., Astron., Fig., Khim.*, No. 3, 211 (1957); *Chem. Abstr.*, **52**, 4391 (1958).

[6] A. M. Lukin and G. B. Zavarikhina, *Zhur. Anal. Khim.*, **13**, 66 (1958).

[7] D. P. Shcherbov and A. I. Ivankova, *Zavodskaya Lab.*, **24**, 667 (1958); *Chem. Abstr.*, **54**, 10662 (1960).

[8] M. Z. Yanpol'skii, *Uchenye Zapiski Kursk. Gosudarst. Pedagog. Inst.*, **1958**, No. 7, 67; *Chem. Abstr.*, **53**, 19692 (1959).

[9] A. M. Lukin and E. A. Bozhevol'nov, *Zhur. Anal. Khim.*, **15**, 43 (1960); *Chem. Abstr.*, **54**, 13970 (1960).

[10] I. P. Alimarin, A. P. Golovina and V. G. Torgov, *Zavodskaya Lab.*, **26**, 709 (1960); *Chem. Abstr.*, **54**, 19298 (1960).

[11] T. Suzuki, *Japan Analyst*, **12**, 655 (1963).

[12] H. S. Frank and R. L. Oswalt, *J. Am. Chem. Soc.*, **69**, 1321 (1947).

[13] S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **73**, 4528 (1951).

contribution of the absorbance caused by the dissociation of the gallium-xylenol orange complex is almost negligible. When the absorbance is measured against a solution containing the same amounts of gallium and xylenol orange, Eq. 2 may be written for the substitution reaction as:

$$\{(D-D_{\mathrm{O}})+x\varepsilon_{\mathrm{C}}\}/\varepsilon_{\mathrm{XO}}=nx \qquad (2)$$

where

$$D=(a-x)\varepsilon_{\mathrm{C}}+(b-na+nx)\varepsilon_{\mathrm{XO}} \qquad (2')$$

$$D_{\mathrm{O}}=a\varepsilon_{\mathrm{C}}+(b-na)\varepsilon_{\mathrm{XO}} \qquad (2'')$$

In these solutions, a and b are the initial concentrations of the gallium-xylenol orange complex and xylenol orange respectively, x is the molar concentration of EDTA added, and ε_{C} and $\varepsilon_{\mathrm{XO}}$ are the molar extinction coefficients of the complex and xylenol orange respectively. If $\{(D-D_{\mathrm{O}})+x\varepsilon_{\mathrm{C}}\}/\varepsilon_{\mathrm{XO}}$ is plotted against x, a straight line with the slope n should be yielded.

In this substitution method, the absorbances were measured by adding various amounts of a 1×10^{-4} M EDTA solution to known amounts of gallium (2.0×10^{-5} M) and xylenol orange (1.0×10^{-4} M), using a blank solution containing the same amounts of gallium and xylenol orange. The pH value was held constant at 5.5. The absorbances were measured at three wavelengths, 400, 410 and 420 mμ, because the difference in absorbance between xylenol orange and the reference solution was the greatest at about 410 mμ. Figure 7 shows the absorption curves of xylenol orange and its gallium complex at pH 5.5 in the wavelength range from 350 to 570 mμ. Curve IV in Fig. 7 is the absorption curve of the complex which is partly shown by curve IV in Fig. 2. The values of ε_{C} were evaluated at the three wavelengths by assuming a 1 to 2 complex, employing the method described by Klotz and LohMing.[14] All the curves are good straight lines with a slope of 2. As a representative result, the values of $\{(D-D_{\mathrm{O}})+x\varepsilon_{\mathrm{C}}\}/\varepsilon_{\mathrm{XO}}$ are plotted in Fig. 8, from which it may be easily understood that a 1 to 2 complex is formed between gallium and xylenol orange.

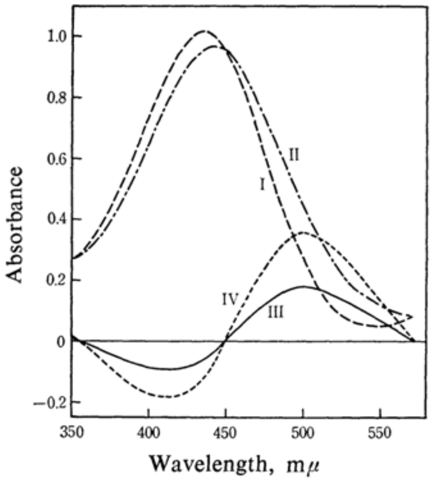

Fig. 7. Absorption curves of XO and its gallium complex at pH 5.5.
I: 0.80×10^{-4} M XO vs. water
II: (0.80×10^{-4} M XO + 1.0^{-5} M (Ga) vs. water
III: (0.80×10^{-4} M XO + 1.0×10^{-5} M (Ga) vs. reagent blank
IV: (1.60×10^{-4} M XO + 2.0×10^{-5} M (Ga) vs. reagent blank

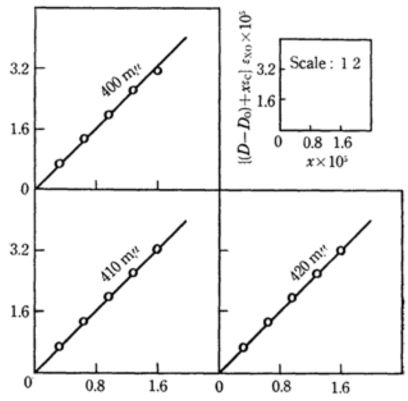

Fig. 8. Plots of $\{(D-D_o)+x\varepsilon_{\mathrm{C}}\}/\varepsilon_{\mathrm{XO}}$ vs. x at various wavelengths.
Reference soln: Ga; 2×10^{-5} M,
XO; 1×10^{-4} M, pH; 5.5

Summary

The reaction between gallium(III) and xylenol orange has been studied spectrophotometrically in order to establish the optimum conditions for determining traces of gallium. Depending on the pH value of a solution, gallium(III) reacts with xylenol orange to form two complexes. The 1 to 1 complex which gives a maximum absorbance in the pH range from 1.2 to 1.7 has an absorption maximum at 530 mμ when measured against a reagent blank. The 1 to 2 complex which gives the maximum absorbance in the pH range from 4.5 to 5.5 has an absorption maximum at 502 mμ. Either with 1 to 1 and 1 to 2 complexes, Beer's law is obeyed up to 60 mμ. of gallium. The apparent molar extinction coefficients of the 1 to 1 and the 1 to 2 complexes have been calculated to be 22900 and 16300 respectively. The present method is comparable in sensitivity with the stilbazo or the luminogallion

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14) I. M. Klotz and W.-C. LohMing, ibid., 75, 4159 (1953).

IREA method. The addition of a small amount of fluoride is effective in eliminating some interfering cations, including aluminum(III), thorium(IV) and zirconium(IV).

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