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The Extraction of Gallium and the Direct Spectrophotometric Determination in the Organic Phase with 4-(2-Pyridylazo)-resorcinol

Kenji BANSHO and Yoshimi UMEZAKI

Resources Research Institute, Kawaguchi, Saitama

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A rapid method for the spectrophotometric determination of microgram amount of gallium with 4-(2-pyridylazo)-resorcinol (PAR) in the organic phase after the extraction of gallium from a hydrochloric acid solution with isopropyl ether and butyl acetate will be described. A red color is formed in an aliquot of the organic extract by the addition of PAR, pyridine, and sodium acetate in methanol. The complex formed in the organic phase has a maximum absorbance at 510 mμ. The color reaction conforms to Beer's law, and the molar absorptivity of the complex is estimated to be approximately 100000. The coefficient of the variation of the absorbance measurements on a standard gallium solution at 510 mμ was about 0.8%. A study of the effect of diverse ions showed the method to be highly selective.

Recently, various chromogenic reagents which are sensitive to gallium, such as Rhodamine B,[1] brilliant green,[2] 1-(2-pyridylazo)-2-naphthol (PAN),[3] and 4-(2-pyridylazo)-resorcinol (PAR),[4,5] have been used for the spectrophotometric determination of gallium. In particular, PAR is very sensitive to gallium, having a molar absorptivity as large as 102000 according to Hagiwara *et al.*[4] Since PAR, however, forms colored species with various metal ions under conditions similar to those holding for gallium, it is necessary to separate gallium from the interfering ions by tedious and time-consuming processes, such as extraction, stripping into an aqueous solution, and the evaporation of the organic solvents, prior to its spectrophotometric determination in the aqueous medium.

The application of PAN as a chromogenic reagent in the organic phase was reported by Rolf[6] for the spectrophotometric determination of zirconium after dibutyl phosphate extraction.

This paper will describe a rapid spectrophotometric determination of gallium with PAR in the organic phase after the extraction of gallium from a hydrochloric acid solution using a mixed solvent of isopropyl ether and butyl acetate.

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[1] K. Nishimura and T. Imai, *Bunseki Kagaku (Japan Analyst)*, **13**, 518 (1964).

[2] K. Hagiwara, M. Nakane, Y. Osumi, E. Ishii and Y. Miyake, *ibid.*, **10**, 1374 (1961).

[3] T. Suzuki, *ibid.*, **12**, 655 (1963).

[4] K. Hagiwara, M. Nakane, Y. Osumi, E. Ishii and Y. Miyake, *ibid.*, **10**, 1379 (1961).

[5] M. Hnilickova and L. Sommer, *Z. Anal. Chem.*, **193**, 171 (1963).

[6] R. F. Rolf, *Anal. Chem.*, **33**, 125 (1961).

Experimental

Apparatus. Absorbance measurements were made with a Hitachi recording spectrophotometer, Model EPS-3, using 1-cm glass cells.

Reagents. *Standard Gallium Solution.* A stock solution containing 100 μg of gallium per m*l* was prepared by dissolving gallium oxide in aqua regia, followed by the fuming-off of nitric acid with hydrochloric acid; then the residue was dissolved in amounts of hydrochloric acid enough to give approximately 0.5 N hydrochloric acid solutions. Standardization was made by titration with a 0.01 M EDTA solution. This solution was diluted as required.

Extractant. A mixture of isopropyl ether and butyl acetate (1 : 1, in vol) was prepared.

PAR Solution. A 0.05% solution was prepared by dissolving 0.05 g of 4-(2-pyridylazo)-resorcinol and 0.5 g of sodium acetate trihydrate in methanol to give 100 m*l* of a solution.

Reducing Agent Solution. A 17% titanium trichloride in an approximately 6 N hydrochloric acid solution, commercially available, was used.

Diluent. A diluent was prepared by dissolving 1 g of sodium acetate trihydrate and 0.3 g of sodium diethyldithiocarbamate in methanol to give 100 m*l* of a solution.

Procedure. In a 50-m*l* separatory funnel, there were placed 10.0 m*l* of a sample solution containing less than 10 μg (preferably 2 to 8 μg) of gallium in approximately 7 N of hydrochloric acid. Add 1 m*l* of the reducing agent solution, and mix by swirling. Add 10.0 m*l* of the extractant, and shake vigorously for 1 min. After the phase separation, remove and discard the aqueous layer. Wash the organic phase for 1 min with a washing solution composed of 10 m*l* of 7 N hydrochloric acid and 1 m*l* of the reducing agent solution. Then again wash the organic phase with two 5-m*l* portions of 7 N hydrochloric acid for 30 sec each. Transfer 5.0 m*l* of the extract into a 10-m*l* volumetric flask. Add 1.0 m*l* of a 0.05% PAR solution and 0.2 m*l* of pyridine successively, and then dilute to the mark with the diluent. After the solution had stood for 10 min, measure the absorbance at 510 mμ against a blank.

Results and Discussion

Extractant. Among the selective extractants for gallium from a hydrochloric acid solution, isopropyl ether seems to be the most promising for the present purposes, because neither ethyl ether[7] nor tributyl phosphate[8] is adequate for the present purposes because of the high volatility of the former and the poor phase-separation of the latter. Nevertheless, a preliminary test with isopropyl ether revealed that this extractant is still too volatile to use for the spectrophotometric determination. In attempt to minimize a possible change in gallium concentration by the volatilization of the solvent during the procedure, a mixture of isopropyl ether and butyl acetate (1 : 1, in vol.) was tried. The extraction of gallium with this extractant was comparable to that with isopropyl ether alone, and the extracts was suitable for the following color development.

Absorption Spectra. The gallium-PAR complex formed in the organic phase is similar to that obtained in an aqueous solution. The absorption spectra are essentially identical, except that the absorbance peak occurs at 510 mμ in this medium, while it appears at 504 mμ in the aqueous medium. From the close resemblance of these spectra, it may be inferred that the metal-ligand ratio of the complex in this medium is 1 : 2, as it is in the aqueous medium.

PAR Concentration. As Fig. 1 shows, 0.5 m*l* of a 0.05% PAR solution is sufficient for the full color development; 1.0 m*l* was used in practice.

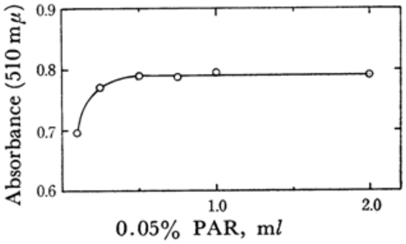

Fig. 1. Effect of PAR
9.46 μg of Ga present in aq. soln.

Effects of Sodium Acetate and Pyridine. When a PAR solution is added to the extract, no color develops because of the interference by the acid extracted simultaneously. According to Hagiwara *et al.*, the optimum pH range for the color development of the gallium-PAR complex in the aqueous medium is between 6 and 8. In this organic medium, therefore, it is necessary to neutralize the acid in order to ensure a stable, full-color development. For this purpose, the applicabilities of bases and salts, such as pyridine, acetates, benzoates, and borates, were compared; finally, sodium acetate and pyridine were chosen, because these compounds are soluble to some extent in the solvents used and, at the same time, have fairly large buffering abilities.

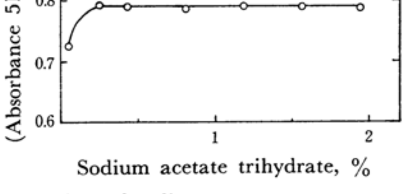

Fig. 2. Effect of sodium acetate
9.46 μg of Ga present in aq. soln.

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[7] E. B. Sandell, *ibid.*, **19**, 63 (1947).

[8] G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry," John Wiley & Sons, New York (1957), p. 129.

In most cases, a 0.3% sodium acetate trihydrate in the final solution is sufficient for the full color development, as is shown in Fig. 2; about 3.8 m*l* of a diluent which contains 1% of this salt is used in practice. Consequently, the total concentration of sodium acetate trihydrate in the final solution becomes approximately 0.43%, including the salt in PAR solution.

However, a lower absorbance, presumably due to the fairly large amounts of acid brought into the organic phase mechanically, was occasionally observed. For the prevention of this accidental error, it is advisable to use regularly a small amount of pyridine. Since the addition of pyridine in amounts as small as 0.1 m*l* is usually sufficient and since the addition in amounts up to 0.8 m*l* does not have any influence on the color intensity of the complex, 0.2 m*l* of pyridine was used in practice. The addition of more than 1 m*l* of pyridine causes a precipitation of sodium acetate.

The Rate of Reaction and the Stability of the Complex. The color development and the stability of the complex are shown in Fig. 3. When the recommended procedure is used, the maximum color intensity is obtained about 6 min after the addition of the reagents and the absorbance remains essentially constant for at least 2 hr.

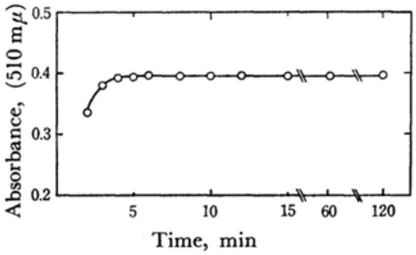

Fig. 3. Color development and stability
4.73 μg of Ga present in aq. soln.

Reduction and Masking. Since several metal ions, including iron(III) and thallium(III), are extracted to some extent under the conditions described and since these ions react with PAR in the organic phase, it is necessary to reduce these ions to lower valencies in which they are indifferent to extraction. Of the reducing agent examined, titanium trichloride was the most effective one in such a strong acid medium as 7 N hydrochloric acid. It was revealed that 1 m*l* of a 17% titanium trichloride solution is necessary for the reduction of ions to the amounts shown in Table 3. However, microgram amounts of titanium and impurities involved in it were sometimes extracted into the organic phase, so causing a positive error. In an attempt to surmount the difficulty, it was found that sodium diethyldithiocarbamate is a proper masking agent under these conditions. As is shown in Fig. 4, a 0.10—0.15% concentration of sodium diethyldithiocarbamate in the final solution can mask up to at least 1 μg of titanium without any influence on the absorbance of the gallium-PAR complex. Therefore, the addition of about 3.8 m*l* of the diluent, which contains 0.3% of sodium diethyldithiocarbamate, in the recommended procedure is sufficient for the complete masking of the titanium brought into the organic phase, which is estimated to be less than 0.5 μg.

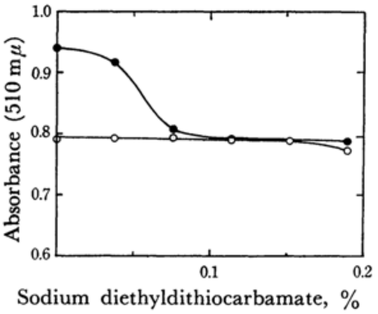

Fig. 4. Masking with diethyldithiocarbamate
9.46 μg of Ga present in aq. soln.
● Approx. 1 μg of Ti present in org. phase
○ No Ti present in org. phase

Effects of the Acidity, Volume, and Temperature of the Aqueous Solution. Since the strict control of the acidity of the sample solution before the extraction is inconvenient for a routine method, the effect of the change in acidity on the color intensity of the complex was examined. As Table 1 shows, a variation of acidity by ±0.5 N corresponds to an error of less than 2%.

On the other hand, the effect of the volume of the sample solution is very small, because the solubility of this extractant is not so large; *i. e.*, 10 m*l* of the extractant decreases in volume to

TABLE 1. EFFECT OF ACIDITY OF AQUEOUS SOLUTION
(4.73 μg of gallium present)

Acidity of aq. solution N	Absorbance
6.5	0.386
6.7	0.386
7.0	0.392
7.3	0.393
7.5	0.393

TABLE 2. EFFECT OF VOLUME OF AQUEOUS SOLUTION
(4.73 μg of gallium present)

Vol. of aq. solution m*l*	Absorbance
5	0.385
7	0.387
10	0.392
13	0.394
15	0.396

Table 3. Effect of diverse ions
(4.73 μg of gallium present)

Ion	Added mg	Ga recovered μg	Error %
Al(III)	10	4.72	−0.2
As(III)	2	4.55	−3.8
	1	4.59	−3.0
Bi(III)	10	4.71	−0.4
Ca(II)	10	4.73	0
Cd(II)	10	4.74	+0.2
Co(II)	10	4.74	+0.2
Cr(III)	10	4.78	+1.1
Cu(II)	10	4.78	+1.1
Fe(III)	2	4.90	+3.6
	1	4.79	+1.3
Ge(IV)	0.5	6.05	+27.9
	0.05	4.85	+2.5
Hg(II)	10	4.79	+1.3
In(III)	10	4.74	+0.2
Mn(II)	10	4.76	+0.6
Mo(VI)	10	4.73	0
Ni(II)	10	4.73	0
Pb(II)	10	4.70	−0.6
Sb(III)	10	4.68	−1.6
Se(IV)	10	4.78	+1.1
Sn(IV)	1	4.90	+3.6
	0.5	4.71	−0.4
Te(IV)	2	4.57	−3.4
	0.5	4.60	−2.7
Tl(III)	2	4.75	+0.4
V(V)	10	4.71	−0.4
U(VI)	10	4.75	+0.4
W(VI)	10	4.71	−0.4
Zn(II)	10	4.73	0
NH_4(I)	50	4.68	−1.6
SO_4^{2-}	50	4.72	−0.2
PO_4^{3-}	50	4.84	+2.3
NO_3^-	1	5.68	+19.8

approximately 9.6 m*l* in a single equilibration with 10 m*l* of 7 N hydrochloric acid. Therefore, a variation of the volume of the sample solution by ±5 m*l* yields an error of less than 2%, as is shown in Table 2.

The temperature dependence of the color intensity is not serious. The volume of the extract incrases with the elevation of the temperature at the rate of about 1% per 5°C; this means a decrease in the color intensity of the complex when an aliquot of the extract is used for color development. On the other hand, the color intensity, in general, has a tendency to increase with the elevation of the temperature. These two factors cancel each other. As a result, a variation in temperature over the 15—25°C range does not have any essential influence on the color intensity.

Beer's Law. Beer's law is obeyed up to at least 5 μg of gallium per 10 m*l* of the final solution. The molar absorptivity of this complex in the medium used was approximately 100000 at 510 mμ. The coefficient of the variation was about 0.8% at a level of 3 μg of gallium per 10 m*l* of the final solution.

Effects of Diverse Ions. The effects of diverse ions on the determination of gallium are summarized in Table 3.

In this method, most common cations do not interfere with the determination of gallium, though several cations, such as arsenic, iron, germanium, tin, and tellurium, serve to limit that determination. Tellurium and selenium produce, upon reduction, precipitates which gather at the intersurface. However, they do not interfere with the determination up to the amounts indicated if the supernatant liquid is used for the color development.

Among the anions tested, nitrate yields a large positive error; this ion must be removed before extraction.