

Summary

1. From equilibrium pressure-composition measurements it has been shown that the primary product of the action of liquid ammonia on tantalum pentachloride is soluble $Ta(NH_2)_2Cl_3 \cdot 7NH_3$ which is deposited from solution, along with the ammonium chloride simultaneously produced, in the form of a light yellow crystalline mass.

2. When heated in a vacuum this compound first loses its seven molecules of ammonia coordinatively bound to form the yellow diamido trichloride of tantalum. Study of this reaction revealed a slight discontinuity at the point where the total ammonia fixed by the solid material was nine moles per gram atom of tantalum present, indicating the formation of the pentamine of the diamido trichloride.

3. By repeated alternate heating and submission to the action of liquid ammonia more than three of the original five chlorine atoms in tantalum pentachloride can be ammonolyzed off to

form a mixture the components of which were of undetermined character.

4. Some properties of $Ta(NH_2)_2Cl_3$ have been described and its thermal decomposition both in the presence of gaseous ammonia and in vacuum studied. In the presence of gaseous ammonia, the first product isolated was the pentanitride while in a vacuum at the same temperature the pentanitride is accompanied by some mononitride and a small amount of a volatile tantalum compound of undetermined composition.

5. At elevated temperature, in either an atmosphere of ammonia or in a vacuum, the pentanitride is found to decompose to the mononitride with the evolution of nitrogen.

6. Tantalum pentanitride has been shown to be crystalline from its X-ray spectrum and its density has been determined.

7. The magnetic constant of tantalum pentachloride has been measured.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Separation of Gallium and its Colorimetric Determination by Means of Quinalizarin¹

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Practically the only method available for the detection and estimation of small amounts of gallium is by means of the spectroscope. This furnishes a specific and sensitive method for detection, and one which in the hands of experienced manipulators is quite accurate for its determination. However, it has the disadvantages of requiring an apparatus which not all laboratories possess, and a technique which everyone has not had an opportunity to develop.

Dennis and Bridgman³ using a spark were able to detect, by means of a direct vision spectroscope, the gallium line, 4172, in a concentration of 3 mg. of gallium per 100 ml. when 0.15 ml. of the solution, corresponding to 0.0046 mg. of gallium, was placed in the small cup used to hold the solution. Approximately five times this amount of gallium

was required for the line 4033 to be visible. The spectrograph has also been employed by Papish and Holt⁴ for the direct detection and semi-quantitative estimation of gallium in certain minerals. Kimura, Nakamura and Kusibe⁵ combined chemical concentration with the spectrographic method for the qualitative examination of a large number of Japanese minerals for gallium.

A colorimetric method, even if not as specific, is desirable and an investigation was, therefore, made to find a dye which would form with gallium, a suitable lake.

Experimental

Aurin tricarboxylic acid, alizarin red-S, titan yellow and quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) were tried. Although the first dye gave a color with small amounts of gallium, as stated by Corey and Rogers,⁶ no suitable experimental conditions could be established which would allow an accurate colorimetric determination.

(1) This manuscript was originally received on August 14, 1933, but was withdrawn and resubmitted after additional experimental work had been done.—EDITOR.

(2) Holder of the J. T. Baker Chemical Company Fellowship in Analytical Chemistry for the Mid-Western Division for the academic year, 1931-1932.

(3) Dennis and Bridgman, *THIS JOURNAL*, **40**, 1531 (1918).

(4) Papish and Holt, *J. Phys. Chem.*, **32**, 142 (1928).

(5) Kimura, Nakamura and Kusibe, *J. Chem. Soc. Japan*, **52**, 55-62 (1931).

(6) Corey and Rogers, *THIS JOURNAL*, **49**, 216 (1927).

Alizarin red-S gave a pink to salmon color in buffered solutions. However, the limits of pH range, from 4.0 to 4.5, were so narrow and the effect of varying concentrations of buffer salts so great that it was practically valueless as a reagent. Titan yellow gave no color with gallium. Quinalizarin gave a pink to amethyst color, depending upon the concentration of gallium and the pH of the solution. Kolthoff⁷ has suggested this last reagent as a sensitive test for aluminum.

Preliminary Investigation of Quinalizarin.—This preliminary work showed that: (a) gallium produced a distinct color in the pH range of 4.5 to 6.0, and that the most favorable condition, considering the effect of aluminum, etc., was a pH of 5.0; (b) the addition of ammonium acetate or ammonium succinate increased the intensity of color of the dye alone and also of solutions containing gallium to about the same extent; (c) the presence of ammonium chloride made the difference in color between the blank and gallium solutions somewhat more pronounced; (d) in general the most uniform results could be obtained if the solutions had a pH of 5 and were normal in ammonium acetate and half normal in ammonium chloride.

Action of Quinalizarin with Other Ions.—Qualitative tests in a solution of pH 5.0, normal in ammonium acetate and half normal in ammonium chloride showed that: iron (Fe^{+++}), tin (Sn^{++}), antimony (Sb^{+++}), copper (Cu^{++}), lead (Pb^{++}), indium (In^{+++}), germanium (Ge^{++++}), vanadyl (VO^{++}), vanadate (VO_3^-) and molybdate (MoO_4^{--}) give colors which are not completely inhibited by fluoride. Iron (Fe^{+++}) and lead (Pb^{++}) cause a blue color while the others are pink. All are very sensitive. Zirconium (Zr^{++++}), thorium (Th^{++++}) and the rare earths give a blue, while tin (Sn^{++++}), beryllium (Be^{++}), aluminum (Al^{+++}), thallium (Tl^{+++}), titanium (Ti^{++++}), arsenite (AsO_3^{--}) and antimonate (SbO_4^{--}) cause a pink color which can be prevented by the addition of fluoride. The alkalis, alkaline earths, magnesium (Mg^{++}), manganese (Mn^{++}), iron (Fe^{++}), mercury (Hg^{++}), thallium (Tl^+), cadmium (Cd^{++}), uranyl (UO_2^{++}), tungstate (WO_4^{--}) and arsenate (AsO_4^{--}) give rise to no color. Silver (Ag^+), mercury (Hg^+), bismuth (Bi^{+++}), tantalum (Ta^{++++}) and columbium (Cb^{++++}), either precipitate as chlorides or hydrolyze out, thus causing no interference after removal by filtration. Cobalt (Co^{++}), nickel (Ni^{++}) and chromium (Cr^{+++}) do not interfere except for their own color. Zinc (Zn^{++}) can be present to the extent of 0.5 g. per liter before any color can be seen. More than that gives an amethyst to blue color.

Influence of Various Acid Radicals on the Color Produced by Gallium (Ga^{+++}), Iron (Fe^{+++}) and Aluminum (Al^{+++}).—Citrate, oxalate and tartrate effectively prevented the formation of color in all cases.

Phosphate had no effect on the color produced by aluminum but prevented the color due to ferric iron if added in sufficient concentration. However, it caused a very appreciable decrease in the color given by gallium.

Fluoride effectively prevented the color given by aluminum, while exerting only a relatively small influence in the case of iron and gallium. The only effect with gallium was a slight decrease in the intensity of color in all solu-

tions, including the blank (see Table I). Experiments showed that 0.5 g. of sodium fluoride per liter, in excess of that required to form Na_2AlF_6 , was necessary for the complete prevention of lake formation by aluminum. This was also about the maximum concentration of sodium fluoride permissible without seriously decreasing the color caused by gallium.

The Limit of Sensitivity for Gallium, Ferric Iron, Aluminum, Zinc and Indium.—This was determined by comparison of 50 ml. of solution in 50-ml. Nessler tubes, 125 mm. to the mark, the source of light being G. E. daylight bulbs, diffused by a ground glass plate. All solutions were *N* in ammonium acetate, 0.5 *N* in ammonium chloride and had a pH of 5.0 \pm 0.1 determined with a quinhydrone electrode. One series contained no sodium fluoride while the other contained 0.5 g. per liter. One ml. of a 0.01% alcoholic solution of quinalizarin was added. The figures given below represent the concentrations of the ions which gave sufficient color to be distinguished with certainty from the blank upon repeated determinations.

TABLE I
LIMIT OF DETECTION OF Ga, Al, Fe^{+++} , Zn AND In WITH QUINALIZARIN

Metal	NaF, 0.5 g./l. metal mg./l.	No NaF, metal mg./l.
Ga	0.02	0.02
Al	20.00	.12
Fe (ic)	0.05	.02
Zn	800.00	400.00
In	10.00	2.00

Since it is obvious that a satisfactory colorimetric determination of gallium is possible only after a separation from many other metals, a study of such separations is described in the following pages. The most difficult and important separations, such as those from aluminum, iron and indium, are so different that they must be treated separately. The usefulness of the method is considerably reduced by the difficulty in removing iron, but many cases are encountered in which only very small amounts of iron are present.

The Determination of Gallium in the Presence of Aluminum

The Influence of Various Salts and pH on the Separation of Aluminum from Gallium by Means of Sodium Fluoride.

—Qualitative and semi-quantitative tests showed that the presence of ammonium chloride, ammonium acetate, the pH of the solution at the time of addition of sodium fluoride, the excess of sodium fluoride and the presence of much sodium or potassium salt influenced the separation of aluminum and the recovery of gallium. Extensive experiments showed that the best separation of aluminum, by precipitation as Na_2AlF_6 , was obtained when sodium fluoride was added as a saturated solution to the solution containing aluminum and gallium which was about half normal in ammonium chloride and buffered with ammonium acetate to a pH of around 5. The presence of more than a few milligrams of potassium or 100 mg. of sodium ion was detrimental to the above separation, although neither potassium nor sodium interfered with the colorimetric part of the determination.

Procedure.—The solution containing gallium and aluminum is neutralized to turbidity with ammonium hy-

(7) Kolthoff, *Chem. Weekblad*, **24**, 447 (1927); *J. Am. Pharm. Assoc.*, **17**, 360 (1928).

droxide, cleared with 6 *N* hydrochloric acid, and 4 ml. in excess added. This is followed by 7.7 g. of ammonium acetate and 2.7 g. of ammonium chloride. (This will make the solution *N* in ammonium acetate, 0.5 *N* in ammonium chloride, and give a *pH* of nearly 5.0 when finally diluted to 100 ml.) After diluting to 70–80 ml. and heating to 70–80°, enough saturated sodium fluoride solution is added, while stirring, to form Na_3AlF_6 and leave 0.5 g. per liter in excess. The resulting precipitate should be of a fine, crystalline nature. If it is of the opalescent, almost invisible type, some of the gallium is practically certain to be retained or else the aluminum may not be removed entirely. When it has stood for one to one and a half hours, with occasional stirring, paper pulp is added, the precipitate filtered off, the filtrate diluted to 100 ml. and adjusted to a *pH* of 5.0 using a quinhydrone electrode. Aliquot portions of such volume as to contain from 0.001 to 0.01 mg. of gallium are placed in 50-ml. Nessler tubes and filled to the mark with the stock solution from which the standards are made. A series of standards is prepared by adding to 50-ml. portions of this solution in Nessler tubes, definite volumes of a standard gallium chloride solution containing 0.01 mg. of gallium per ml. One ml. of a 0.01% alcoholic solution of quinalizarin is added to each tube, the contents stirred and the colors compared after one or two minutes.

Using 50-ml. Nessler tubes, the best concentration for comparison lies between 0.02 and 0.2 mg. of gallium per liter. Between 0.02 and 0.08 mg. per liter, a difference of 0.01 mg. per liter can be detected easily. Above that, it requires a difference of 0.02 mg. per liter.

The quinalizarin solution is not very stable and becomes practically useless after it has been prepared a week. Neither is it much good directly after preparation. It gives the best results from one to four days after preparation.

It is not necessary that the solutions have a *pH* of exactly 5.0, but it is necessary that both standards and unknown have the same *pH*. A very great deviation from 5 is not recommended, however, since at 4.5 the sensitivity of the gallium is much less, while at a higher *pH* the sensitivity of aluminum is greater.

The presence of 0.5 g. of sodium fluoride per liter is to be recommended in all cases, even if a separation of aluminum has not been made, since it will prevent any color due to traces of that element which are almost certain to be present.

The results shown in Table II, numbers 1 to 10, were obtained by the above method, while numbers 11 to 15 were obtained without preliminary separation of aluminum.

From this it is seen that gallium can be separated accurately from aluminum if not more than 10 mg. of the latter is present. If the concentration of aluminum is not greater than 15 mg. per liter, the gallium can be determined directly without a preliminary precipitation of aluminum as Na_3AlF_6 .

The Determination of Gallium in the Presence of Iron and Indium

Since quinalizarin gives a very sensitive color reaction with ferric iron, it is essential that every trace of this ion be removed before proceeding with the colorimetric

TABLE II
DETERMINATION OF GALLIUM IN THE PRESENCE OF ALUMINUM

No.	Al, mg.	Ga taken, mg.	Ga found, mg.	Error, mg.
1	10	0.000	0.000	±0.000
2	10	.005	.0047	— .0003
3	10	.010	.011	+ .001
4	10	.010	.012	+ .002
5	10	.010	.010	± .000
6	10	.020	.021	+ .001
7	10	.050	.047	— .003
8	20	.000	.000	± .000
9	20	.010	.0075	— .0025
10	20	.010	.006	— .004
	Al, mg./50 ml.	Ga taken, mg./50 ml.		
11	0.75	0.000	0.000	±0.000
12	.75	.0005 ^a	.000	— .0005
13	.75	.001	.0011	+ .0001
14	.75	.0025	.0028	+ .0003
15	.75	.005	.005	± .000

^a 0.0005 mg. of gallium in 50 ml. of solution is beyond the limit of sensitivity of the test.

determination of gallium. Experiments showed that it was not possible to convert the iron into ferrocyanide and determine the gallium directly, nor to collect quantitatively the latter from a solution by precipitating it along with cadmium sulfide. When the iron was reduced before adding quinalizarin, it was found that the reducing agents such as bisulfite, hydrazine sulfate and hydroxylamine hydrochloride failed to cause complete reduction. Others, like sodium hydrosulfite and phenylhydrazine hydrochloride, destroyed the dye.

The Separation of Iron and Indium from Gallium by Means of an Excess of Sodium Hydroxide.—Although this is a standard method of separation in ordinary analytical work, two serious difficulties were encountered in this instance. First, the adsorptive properties of ferric hydroxide proved to be so great that more than 1 mg. of iron prevented complete recovery of the gallium. Second, sufficient ferric hydroxide to give a color with the dye remained in the colloidal state and passed through the filter, even though the precipitate was settled by centrifuging, and removed by the method recommended by Cox, Schwartz, Hahn, Unangst and Neal,⁸ for the separation of iron and aluminum. However, the use of hydrated manganese dioxide as a collector according to the method of Stokes and Cain⁹ was found to give entirely satisfactory results for both iron and indium.

Procedure.—The solution containing the iron and gallium in 25 ml. or less, was heated nearly to boiling and enough approximately 3 *N* sodium hydroxide added to make the final concentration between half normal and normal. The heating was continued until the ferric hydroxide had coagulated. Paper pulp was added, the precipitate filtered off and washed with a hot 1% sodium chloride solution made alkaline with sodium hydroxide.

(8) Cox, Schwartz, Hahn, Unangst and Neal, *Ind. Eng. Chem.*, **24**, 403 (1932).

(9) Stokes and Cain, *THIS JOURNAL*, **29**, 409 (1907).

The paper pulp and filter paper used in this, and the next, filtration had been treated with hot 1.5 *N* sodium hydroxide solution and then washed with water. The filtrate was heated nearly to boiling, eight to ten drops of a 1% potassium permanganate solution added, and this followed in a minute or two by enough alcohol (5 to 10 drops) to cause reduction. The heating was continued until all green color had disappeared, and the brown precipitate of hydrated manganese dioxide had formed. This was filtered off and washed as before. The filtrate was neutralized to litmus with hydrochloric acid and enough ammonium chloride, ammonium acetate and sodium fluoride introduced so that the pH of the solution and the salt concentration would have the values previously recommended, when the whole was diluted to the desired volume (100 or 250 ml.). This was most conveniently done by adding the sodium fluoride as a saturated solution, and the other two salts as a stock solution with a pH of 5, which was 1.5 *N* in the former and 3 *N* in the latter.

In the case of indium the precipitate need not be filtered off before adding the permanganate.

The gallium was then determined as described under "The Determination of Gallium in the Presence of Aluminum." Table III shows the results obtained using the above procedure.

TABLE III
THE SEPARATION OF GALLIUM FROM IRON AND INDIUM

No.	Fe, mg.	Ga taken, mg.	Ga found, mg.	Error, mg.
1	0.5	0.010	0.009	-0.001
2	.5	.020	.018	-.002
3	1.0	.000	.000	= .000
4	1.0	.005	.006	+ .001
5	1.0	.020	.020	= .000
6	1.0	.060	.058	-.002
7	2.0	.010	.005	-.005
8	2.5	.010	.008	-.002
9	20.0	.010	.003	-.007
10	0.0	.010	.009	-.001
11	.1	.010	.010	= .000
12	.2	.000	.000	= .000
13	.2	.005	.0055	+ .0005
14	.2	.010	.012	+ .002
15	.2	.050	.048	-.002
In, mg.				
16	100	.000	.000	= .000
17	100	.010	.011	+ .001
18	100	.025	.028	+ .003
19	100	.050	.052	+ .002
20	100	.060	.058	-.002

In numbers 10 to 20 the precipitate of ferric hydroxide, or indium hydroxide, was not filtered off before adding the potassium permanganate and reducing.

From this it can be seen that gallium can be determined accurately in the presence of iron, using the method given, only when not more than 1 mg. of the latter is present; otherwise a very appreciable amount of the gallium will be lost. Determinations 10 to 15 show that if not more than 0.2 mg. of iron is present, it is unnecessary to filter off the ferric hydroxide before adding the permanganate. With larger amounts of iron, it was found that it was removed in-

completely unless filtered off as recommended in the procedure. Indium gives no difficulty even when 100 mg. is present.

Data obtained, but not included in the table, showed that if the concentration of indium did not exceed 8 mg. per liter, accurate determinations of gallium could be made without a preliminary separation.

The Determination of Gallium in the Presence of Zinc and Aluminum or Iron

Since preliminary determinations, Table I, showed that nearly 600 mg. of zinc per liter gave no color with quinalizarin if 0.5 g. of sodium fluoride was present, no special procedure was necessary for determining gallium in the presence of this element.

With zinc alone, the gallium was determined directly in solutions having a pH and the salt concentrations previously given. (Results are shown in Table IV, numbers 1 to 5.) When zinc and aluminum were both present, the latter was separated by the procedure given under "The Determination of Gallium in the Presence of Aluminum," and the gallium determined as if zinc were absent. (Determinations from 6 to 11 show the results obtained.) With iron and zinc present the procedure given under "The Determination of Gallium in the Presence of Iron" was followed except that sufficient sodium hydroxide was added to dissolve the zinc hydroxide. (Determinations 12 to 15 are representative of the results obtained.)

TABLE IV
THE DETERMINATION OF GALLIUM IN THE PRESENCE OF ZINC AND IRON OR ALUMINUM

No.	Al, mg.	Zn, mg.	Ga taken, mg.	Ga found, mg.	Error, mg.
1		25.0	0.000	0.000	= 0.000
2		25.0	.001	.0012	+ .0002
3		25.0	.005	.006	+ .001
4		50.0	.010	.010	= .000
5		50.0	.020	.020	= .000
6	10.0	20.0	.000	.000	= .000
7	10.0	10.0	.005	.006	= .001
8	10.0	20.0	.025	.023	-.002
9	0.25	12.5	.003	.0035	+ .0005
10	.25	12.5	.010	.009	-.001
11	.50	20.0	.030	.035	+ .005
Fe, mg.					
12	1.0	20.0	.000	.000	= .000
13	1.0	20.0	.005	.004	-.001
14	1.0	100.0	.025	.024	-.001
15	1.0	200.0	.060	.065	+ .005

Numbers 4, 5, 10, 11, 14 and 15 were diluted to 100 ml. and aliquots taken for colorimetric comparison. In determinations 6, 7 and 8 the Na_3AlF_6 was filtered off before comparison, while in 9, 10 and 11 the comparison was made without prior filtration.

This shows that gallium can be determined in the presence of zinc if the ratio of zinc to gallium does not exceed 25,000 to 1, providing the solution contains 0.5 g. of sodium fluoride per liter. If the Na_3AlF_6 was not filtered off, as in determinations 9, 10 and 11, a color was produced if approximately the maximum amounts of both zinc and aluminum, which would give no color when alone, were pres-

ent, but not when half that quantity of each element was present.

The Determination of Gallium in the Presence of Iron and Aluminum

It was not possible to precipitate the aluminum with sodium fluoride, after the separation of iron with an excess of sodium or potassium hydroxide, due to the interference of the large amount of alkali salts introduced. This made it necessary to acidify the solution after the removal of iron and precipitate the hydroxides of gallium and aluminum by ammonium hydroxide. If this precipitate was filtered on the best grade of filter paper it was found that traces of iron were extracted from the paper during the boiling with hydrochloric acid necessary to redissolve the hydroxides. To avoid this interference the solution was filtered through a Gooch crucible containing a mat of purified anthracene or phenanthrene.^{10,11}

Procedure.—The iron was separated as described under "The Determination of Gallium in the Presence of Iron and Indium" and the filtrate acidified with hydrochloric acid. The aluminum and gallium hydroxides were precipitated with ammonium hydroxide according to Blum's method¹² and filtered through a Gooch crucible containing an anthracene or phenanthrene mat, supported on a perforated disk. The precipitate and mat were transferred to the original beaker and boiled with hydrochloric acid. The filtering medium was filtered off through a paper previously washed with 5 *N* hydrochloric acid. The aluminum was then separated by means of sodium fluoride and the gallium determination completed in the usual manner. If only a half milligram of aluminum or less was present, the gal-

lium was determined directly without any separation from that element. The results are shown in Table V.

It is therefore possible to determine gallium in the presence of iron and aluminum when both of the latter are present in as large an amount as is permissible when either is present alone.

The Determination of Gallium in the Presence of Lead, Copper, Tin, Antimony, Germanium and Platinum

Procedure.—The strongly hydrochloric acid solution containing the above elements was distilled to remove germanium. The acidity of the remaining solution was adjusted so as just to prevent precipitation by hydrolysis, and stirred with a small excess of cadmium metal (40 to 60 mesh). The precipitated metals and excess of cadmium were filtered off, 2 to 3 ml. of concd. sulfuric acid added to the filtrate and evaporated to fumes to expel hydrochloric acid. Approximately 100 ml. of water was added and the cadmium removed by electrolysis. This was followed by treatment with hydrogen sulfide to remove the last traces of cadmium and any of the other metals which might be remaining. After filtration and washing, the filtrate was reduced in volume by evaporation, treated with an excess of sodium hydroxide, potassium permanganate, etc., and the determination completed as previously given.

By this method 0.01 mg. of gallium could be determined in the presence of 0.1 g. of each of the above metals either singly or as a mixture.

TABLE VI

THE DETERMINATION OF GALLIUM IN THE PRESENCE OF LEAD, COPPER, TIN, ANTIMONY, GERMANIUM AND PLATINUM

No.	Milligrams	NUM		Error, mg.
		Ga taken, mg.	Ga found, mg.	
1	Pb 100	0.000	0.000	±0.000
2	Pb 100	.010	.012	+ .002
3	Pb 100	.100	.090	- .010
4	Cu 100	.000	.000	± .000
5	Cu 100	.010	.010	± .000
6	Cu 100	.050	.050	± .000
7	Sn 100	.000	.000	± .000
8	Sn 100	.010	.012	+ .002
9	Sn 100	.050	.053	+ .003
10	Sb 100	.000	.000	± .000
11	Sb 100	.010	.011	+ .001
12	Sb 100	.050	.045	- .005
13	Sn 100 Sb 100	.000	.000	± .000
14	Sn 100 Sb 100	.010	.010	± .000
15	Sn 100 Sb 100	.050	.048	- .002
16	Pb 100 Cu 100	.000	.000	± .000
17	Pb 100 Cu 100	.010	.008	- .002
18	Pb 100 Cu 100	.100	.105	+ .005
19	Ge 30	.000	.000	± .000
20	Ge 30	.010	.008	- .002
21	Ge 30	.100	.107	+ .007
22	Ge 30	.000	.000	± .000
23	Ge 30	.010	.011	+ .001
24	Ge 30	.050	.050	± .000
25	Pt 20	.000	.000	± .000
26	Pt 20	.010	.012	+ .002
27	Pt 20	.050	.053	+ .003

In numbers 22, 23 and 24 the germanium was separated by precipitation as the sulfide.

TABLE V

SEPARATION OF GALLIUM FROM ALUMINUM AND IRON

No.	Al, mg.	Fe, mg.	Ga taken, mg.	Ga found, mg.	Error, mg.
1	10.0	1.0	0.000	0.000	±0.000
2	10.0	1.0	.005	.006	+ .001
3	10.0	1.0	.020	.020	± .000
4	10.0	1.0	.050	.045	- .005
5	15.0	1.0	.010	.008	- .002
6	1.0	1.0	.010	.008	- .002
7	0.5	1.0	.000	.000	± .000
8	.5	1.0	.005	.0055	+ .0005
9	.5	1.0	.010	.008	- .002
10	.5	1.0	.050	.045	- .005
11	.5	1.0	.030	.030	± .000

In Nos. 1-6, the Na_2AlF_6 was filtered off. In Nos. 7-11 no separation of the aluminum was made. Nos. 3, 4, 5, 6, 9, 10 and 11 were diluted to 100 ml. and aliquots taken for comparison.

(10) Gooch, *Proc. Am. Acad. Arts Sci., New Series*, **12**, 390 (1884-85).

(11) These latter substances were purified by dissolving in hot acetone and pouring slowly with constant agitation into an equal volume of concentrated hydrochloric acid. The precipitated anthracene or phenanthrene was filtered off and washed first with hot dilute hydrochloric acid and then with hot water. It was then crystallized from acetone or toluene. If this product, when boiled with hydrochloric acid, gave an extract which produced a color with quinalizarin under the conditions of the colorimetric determination, the process was repeated.

(12) Blum, *This Journal*, **38**, 1282 (1916).

A direct precipitation of more than a trace of the sulfide metals with hydrogen sulfide from a 0.3 *N* acid solution usually resulted in loss of gallium due to its being carried down with the sulfide precipitate, except with the small amount of germanium which was present. In this case, a quantitative separation was obtained by precipitating this element with hydrogen sulfide from 6 to 8 *N* hydrochloric acid. Results obtained are shown in Table VI.

General Procedure.—Obtain the substance in a hydrochloric acid solution and filter off any silver, lead and mercurous mercury which may have precipitated as chloride. Follow this by the procedure given under "The determination of Gallium in the presence of Lead, Copper, Tin, Antimony, Germanium and Platinum." Next separate iron, indium and aluminum, and determine gallium according to the procedure given under "The determination of Gallium in the presence of Iron and Aluminum." This will remove all interfering elements except vanadium and molybdenum, for which no satisfactory separation was found. As much as 100 mg. of lead, copper, antimony, tin, zinc, indium and doubtless that much platinum and germanium may be present,

but more than 10 mg. of aluminum and one milligram of iron cause difficulty.

Summary

1. A method for the colorimetric determination of gallium has been developed, based upon the formation of a pink to amethyst colored lake with quinalizarin. The optimum condition is a solution which is normal in ammonium acetate, 0.5 *N* in ammonium chloride, of *pH* 5.0 and containing 0.5 g. of sodium fluoride per liter. Under these conditions 0.02 mg. of gallium per liter can be distinguished. The best concentrations for comparison, using 50-ml. Nessler tubes, lie between 0.02 and 0.2 mg. of gallium per liter.

2. Methods have been developed for separating minute amounts of gallium from 100 mg. of those metals which interfere by giving colored lakes under the same conditions, namely, lead, copper, tin, antimony, indium, platinum and germanium, except that not more than 10 mg. of aluminum, nor 1 mg. of iron should be present, while vanadium and molybdenum must be absent.

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The Hydration of Unsaturated Compounds. IV. The Rate of Hydration of Isobutene in the Presence of Silver Ion. The Nature of the Isobutene-Silver Complex¹

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It has been shown that certain soluble metallic salts, such as those of copper, nickel, manganese, etc., have little or no effect upon the rate with which dilute nitric acid catalyzes the hydration of isobutene,² whereas in the presence of mercuric nitrate only the isobutene which is not combined with the mercury undergoes hydration. A similar study of the hydration of isobutene in the presence of silver ion is of interest, not only from the theoretical but also from the practical point of view, since silver salts are often added to acids in order to aid the absorption of olefins.

In order to interpret the experimental data obtained from the hydration of isobutene in the presence of silver ion, it is necessary to know the nature of the silver-isobutene complex and the value of the hydration constant of isobutene in

the absence of silver ion. The latter is already known.²

Nature of the Silver-Isobutene Complex.—This was determined by measuring the distribution ratio of isobutene between, first, carbon tetrachloride and aqueous potassium nitrate, and, second, between carbon tetrachloride and aqueous silver nitrate. In these measurements the ionic strength was maintained constant at 1 *N* by adjusting the concentration of potassium nitrate. In addition to these data, the distribution ratios of isobutene between carbon tetrachloride and pure water, and between carbon tetrachloride and 2 *N* potassium nitrate were also determined. The experimental results are shown in Tables I and II. All concentrations are expressed in moles per liter of solution.

In developing the expressions for the formation of the complex between butene and silver ion,

(1) For the previous publication in this series, see Lucas and Liu, *THIS JOURNAL*, **56**, 2138 (1934).

(2) Lucas and Eberz, *ibid.*, **56**, 460 (1934).