

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A GRAVIMETRIC METHOD FOR THE SEPARATION AND DETERMINATION OF TITANIUM¹

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Existing methods for the separation of titanium from its common associates leave much to be desired from the standpoint of accuracy, ease of manipulation and speed. A perusal of the monograph "Titanium" by William M. Thornton is convincing evidence that a method for the determination of titanium in the presence of other elements, which avoids long and tedious separations and does not produce a gelatinous precipitate, is greatly needed.

Under proper conditions, a crystalline salt of titanium is quantitatively precipitated by potassium iodate, no precipitate being produced with aluminum, calcium, magnesium, nickel, phosphorus and chromium, elements which are commonly associated with titanium in ores. With slight modifications the method effects a separation of titanium from zirconium and manganese. It is necessary, however, that iron be removed previous to the determination of titanium. This is readily accomplished without modification of the method in any essential.

Reagents and Solutions

Titanium.—Titanium sulfate solutions were prepared by dissolving twice recrystallized potassium fluotitanate in sulfuric acid and heating to dense fumes of sulfur trioxide. Water was then added to obtain the desired concentration and the solutions were standardized by the precipitation of titanium hydroxide with ammonium hydroxide. The solutions used contained approximately 0.1 g. of TiO_2 in 50 cc. of solution and were 1.2 *N* with respect to sulfuric acid.

Zirconium.—A solution of c. p. zirconium nitrate which was 0.3 *N* with respect to sulfuric acid was prepared and standardized by precipitation with ammonium hydroxide. The solution was tested qualitatively and found to be free from iron and titanium. The hafnium content of this solution is not known and was not investigated.

Other Elements.—Solutions of the following c. p. salts, alum, calcium chloride, magnesium chloride, nickel chloride, iron chloride, manganous sulfate, primary potassium phosphate (recrystallized), ammonium vanadate, sodium chromate, were used as sources of these elements.

Potassium Iodate.—C. p. grade.

Thirty per cent. Hydrogen Peroxide.—Merck's Superoxol.

The Quantitative Determination of Titanium.—The procedure for the determination of titanium, employing the optimum conditions, follows. To 50 cc. of the standard solution, there was added 27 cc. of concentrated nitric acid and the volume made up to 200 cc. The reagent was prepared

¹ From the thesis submitted by Dorothea R. Mossman in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1930. Original manuscript received August 29, 1931.

by dissolving 10 g. of potassium iodate in 100 cc. of water containing a few drops of nitric acid. This small concentration of nitric acid prevents the precipitation of potassium iodate when the solution cools. The reagent was added to the titanium sulfate solution slowly and with stirring, at room temperature. The precipitate was allowed to stand for about one hour, stirring now and again until the iodate precipitate changed from a flocculent to a dense crystalline form, and then it was washed five times by decantation with 20-cc. portions of a 2% solution of potassium iodate which contained 6 cc. of concentrated nitric acid to every 100 cc. of solution. The filter paper and precipitate were then transferred to the original beaker, 15 cc. of concentrated hydrochloric acid added and the filter paper macerated by the use of a stirring rod. A small volume of water was then added and sulfur dioxide bubbled through the solution until the brown coloration which first formed had completely disappeared. The volume was then adjusted to about 300 cc. and the sulfur dioxide expelled by boiling. The titanium was then precipitated by ammonium hydroxide, filtered, washed, ignited and weighed as titanium dioxide.

Determinations 1 through 20 of Table I show the results obtained when this procedure was followed. Determinations 21 through 35 show the results obtained when acids other than nitric and normalities other than 1.6 were used. Determinations 36 through 41 show the application of this method in determining amounts of titanium dioxide other than 0.1 g.

TABLE I
EXPERIMENTAL DATA

No.	Approx. wt. TiO ₂ , g.	Acid, cc.	Added acid	Total normality acid	KIO ₃ added, g.	Number of analyses	Av. dev., %	Max. dev., %	Dev. of av. from standard, %
1-20	0.12	27	HNO ₃	1.6	10	20	0.1	0.3	+0.01
21-22	.12	13	H ₂ SO ₄	1.7	10	2	.1	.1	+ 2
23-24	.12	27	HCl	1.6	10	2	.05	.05	+ .05
25-26	.12	15	HNO ₃	1.0	10	2	.05	.05	+ .05
27-28	.12	7	H ₂ SO ₄	1.0	10	2	.2	.2	+ .1
29-30	.12	15	HCl	1.0	10	2	.05	.05	+ .15
31-33	.12	5.5	H ₂ SO ₄	0.9	10	3	.03	.1	+ .1
34-35	.12	None added		.2	10	2	.05	.05	+ .05
36-37	.2	27	HNO ₃	1.6	15	2	.02	.02	- .07
38-39	.05	27	HNO ₃	1.6	10	2	.2	.2	.00
40	.01	27	HNO ₃	1.6	10	1			1.0
41	.01	27	HNO ₃	1.6	15	1			0.00

When the iodate precipitation was performed in solutions of greater acidity than those given in the table, addition of ammonium hydroxide to the filtrate showed the presence of titanium. Hence in solutions whose acid concentration is appreciably greater than 1.7 normal, the precipitation of titanium is incomplete.

It appears advisable when determining amounts of titanium dioxide very much greater or very much less than 0.1 g. to increase the quantity of potassium iodate added, in order to ensure rapid precipitation. Thus, in determination 40 of the above table, the precipitation, while complete, appeared only after standing for several days, whereas in determination 41 the precipitate appeared immediately in the dense very insoluble crystalline form.

Separation from Other Elements

Aluminum, Calcium, Magnesium and Nickel.—Preliminary tests having shown that aluminum, calcium, magnesium and nickel were not precipitated under the conditions of the determination, the maximum weight of the oxides of these elements that could be present without causing interference was then ascertained.

The separation of titanium from these elements using a single precipitation was accomplished by employing the iodate method as outlined above. In those determinations involving a second precipitation, the iodate precipitate was washed back into the original beaker with hot water, 25 cc. of concentrated hydrochloric acid was added and sulfur dioxide bubbled through the solution until the brown coloration disappeared. The sulfur dioxide was then completely expelled by boiling, the volume adjusted to 200 cc. and the titanium reprecipitated by the addition of 10 g. of potassium iodate dissolved in 100 cc. of water. From this point the procedure was similar to that already described. Table II shows the results thus obtained.

TABLE II
EXPERIMENTAL RESULTS

Approx. wt. of TiO ₂ , g.	No. of pptns.	Interfering element, g.	Number of analyses	Av dev., %	Max. dev., %	Dev. of av. from standard, %
0.1	1	0.1-0.2 Al ₂ O ₃	9	0.1	0.3	-0.05
.1	1	.25 Al ₂ O ₃	2	.05	.05	+ .35
.1	2	.35 Al ₂ O ₃	4	.2	.3	+ .2
.1	1	.1 CaO	6	.1	.2	- .1
.1	1	.12-0.15 CaO	2	.15	.15	+ .6
.1	2	.2 CaO	4	.2	.3	+ .2
.1	1	.2-1.0 MgO	6	.1	.2	- .1
.1	1	.4 NiO	4	.15	.2	+ .1

The above results show that an accurate separation of 0.1 g. of TiO₂ from 0.2 g. of Al₂O₃, from 0.1 g. of CaO, from 0.4 g. of NiO and from very large amounts of MgO may be obtained. When a double precipitation is employed, the permissible quantity of Al₂O₃ and of CaO is increased to 0.35 g. and 0.2 g., respectively. The presence of larger quantities of the interfering elements than those shown in the table resulted in adsorption and consequent high results for the titanium oxide content.

Phosphorus, Vanadium and Chromium.—Phosphorus is frequently and vanadium and chromium occasionally are encountered in the analysis of titanic materials. Chromium, equivalent to 0.07 g. of CrO_3 , did not produce a precipitate under the conditions of the determination. Vanadium, equivalent to 0.05 g. of V_2O_5 , produced a bright red precipitate. However, 1 mg. of V_2O_5 , which is as much as is likely to be present in a titanium ore, did not produce a precipitate. The iodate precipitation separated titanium from phosphorus very effectively as the results in Table III show.

TiO ₂ taken, g.	TiO ₂ found, g.	P ₂ O ₅ present, g.
0.1023	0.1024	0.025
	.1024	.040
	.1020	.040

Manganese.—Manganese is not precipitated by potassium iodate under the conditions of the experiment but a slight brown deposit, which appears to be manganese dioxide, forms in the course of an hour.

An attempt was made to keep the manganese in solution by observing Blum's precautions when precipitating with ammonium hydroxide, and results 1, 2 and 3 of Table IV were obtained. These results, therefore, corroborate Blum's statement² that oxidation and precipitation of manganese occurs so rapidly as to preclude quantitative separation and are in disagreement with the work of Lundell and Knowles.³

Correct results were obtained when the following procedure was used. The iodate precipitate was washed back into the original beaker by a stream of hot water and its solution effected by means of hydrochloric acid and sulfur dioxide; 1 cc. of a saturated ammonium bisulfite solution was added and the titanium then precipitated by the basic acetate method. Determinations 4 and 5 show the results obtained when 10 milligrams of Mn_3O_4 was present.

No.	TiO ₂ taken, g.	TiO ₂ found, g.	Mn ₃ O ₄ present, g.
1	0.1162	0.1186	0.020
2		.1169	.010
3		.1192	.010
4	.1147	.1148	.010
5		.1145	.010

Iron.—Iron, in small quantities, is completely precipitated by potassium iodate under the conditions of the experiment. When larger quantities of iron are present (*e. g.*, 0.1 g. of Fe_2O_3), the iron is incompletely precipitated. It was therefore necessary to remove iron previous to the precipitation of titanium, by Rothe's ether method, the modifications

² W. Blum, "Scientific Papers of the Bureau of Standards," No. 286, 1916.

³ G. E. F. Lundell and H. B. Knowles, *THIS JOURNAL*, 45, 676 (1923).

employed being those described by Barnebey and Isham,⁴ Three ether extractions were performed. The aqueous layer was then transferred to a beaker, warmed to remove ether, and evaporated to 50 cc. to adjust the acid concentration. The volume was then brought to 200 cc. and the titanium precipitated as iodate. After the titanium iodate had changed form, it was washed as in the regular procedure, filtered, and washed back into the original beaker by means of hot water; 15 cc. of hydrochloric acid was added and sulfur dioxide bubbled in to effect the solution of the iodate precipitate. The excess sulfur dioxide was then expelled by boiling and the titanium precipitated by the basic acetate method using ammonium bisulfite to maintain the trace of iron, still remaining, in the reduced condition.⁵ By means of this procedure the results in Table V were obtained.

TABLE V

No.	TiO ₂ taken, g.	TiO ₂ found, g.	Fe ₂ O ₃ present, g.
1	0.1147	0.1148	0.12
2	.	.1146	.12
3	.	.1148	.2
4	.	.1149	.2
5	.	.1149	.2
6	.	.1145	.2
7	.	.1145	.2
8	.	.1148	.2
9	.	.1149	.2
10	.	.1147	.2
11	.	.1146	.2

Zirconium.—Existing methods for the separation of titanium and zirconium were found unsatisfactory. Davis⁶ has given a few results on the use of sodium iodate as a precipitating reagent for zirconium in a nearly neutral solution, claiming that even in the presence of small quantities of acid the precipitation was incomplete. Because of the sensitivity of this reaction to slight changes in acidity, this method has been useless for practical purposes. Since Davis specifies merely an excess of sodium iodate, it was thought that this reaction might be used for quantitative purposes if as much as 10 g. of potassium iodate were used.

Zirconium was found to be partially precipitated by potassium iodate when the regular procedure, using a solution of acid normality 1.6, was employed. However, the precipitation was found to be complete in a solution which was 0.3 normal in respect to sulfuric acid. The iodate precipitate was redissolved by hydrochloric acid and sulfur dioxide and the zirconium reprecipitated by ammonium hydroxide. Determinations 1 through 4 of Table VI show the results obtained when this procedure was followed.

⁴ O. L. Barnebey and R. M. Isham, *THIS JOURNAL*, **32**, 957 (1910).

⁵ Wm. M. Thorton, *Am. J. Sci.*, [4] **37**, 173 (1914).

⁶ I. Thomas Davis, *Am. Chem. J.*, **11**, 26 (1889).

Determinations 5 through 10 show analyses of solutions containing both titanium and zirconium. To these solutions 35 cc. of Superoxol was added and the volume made up to 200 cc.; 100 cc. of water containing 10 g. of potassium iodate was added to the solution and the precipitate allowed to stand for about three hours. The slight reaction which occurs between the hydrogen peroxide and the potassium iodate in no way interferes with the determination. After standing for three hours, the zirconium precipitate was filtered through a porcelain filter crucible and washed by decantation with 150 cc. of water containing 3 g. of potassium iodate and 3 cc. of Superoxol. Nine cc. of sulfuric acid was then added to the filtrate and the hydrogen peroxide expelled by boiling. An inverted funnel was suspended over the beaker to prevent loss by effervescence. When the hydrogen peroxide had been expelled the titanium precipitate appeared. The evaporation was continued down to a volume of 300 cc., when the beaker was removed from the flame and allowed to cool with occasional stirring. The remaining operations for the determination of titanium were the same as those already described.

In order to determine the zirconium, the precipitate was dissolved through the porous bottomed crucible by means of concentrated hydrochloric acid, followed by water. Sulfur dioxide was then bubbled through the solution for a minute or two and the excess sulfur dioxide expelled by boiling. Macerated filter paper was then added to the solution, the zirconium precipitated by ammonium hydroxide, washed with hot 2% ammonium nitrate solution, filtered and ignited to the oxide.

When more than 10 milligrams of zirconium dioxide was present it was found that the zirconium precipitate absorbed titanium to a large extent. However, since zirconium occurs only in small quantities in titanium ores, this method will be found applicable.

TABLE VI

No.	TiO ₂ taken, g.	TiO ₂ found, g.	ZrO ₂ taken, g.	ZrO ₂ found, g.
1			0.0150	0.0150
2				.0150
3			.0100	.0100
4				.0101
5	0.1023	0.1023	.0100	.0100
6		.1025		.0100
7		.1024		.0101
8		.1021		.0101
9		.1022		.0100
10		.1023		.0099

Determination of the Composition of the Iodate Precipitate.—Since there is no mention in the literature of a compound containing titanium and the iodate radical it was decided to determine, if possible, the composition of the precipitate.

The precipitate was washed about twenty times with pure water, in which it is insoluble. Difficulty was experienced in drying the precipitate as a slight decomposition with simultaneous discoloration of the compound took place very readily. However, one product which was fairly white was obtained by drying over phosphorus pentoxide in a vacuum for several days and another was obtained by drying in the oven at 60° to constant weight.

Weighed portions of the precipitate so prepared were used to determine the titanium and iodate content. Titanium was determined by basic acetate precipitation. Iodate was determined by reduction with potassium iodide and titration of the liberated iodine by sodium thiosulfate solution.

The results, which indicate that the compound is a double salt of formula $Ti(IO_3)_4 \cdot 3KIO_3$, are shown below

% Titanium found	% Iodate found
3.48 (dried over P_2O_5)	87.39 (dried over P_2O_5)
3.58 (dried over P_2O_5)	
3.56 (dried in oven)	88.32 (dried in oven)
3.40 (dried in oven)	88.35 (dried in oven)
Av. 3.50%	Av. 88.02%
Titanium calculated, 3.46%	Iodate calculated, 88.10%

Summary

A new gravimetric method for the determination of titanium has been described, in which the titanium is precipitated as a double potassium titanium iodate whose probable composition is $Ti(IO_3)_4 \cdot 3KIO_3$. The new method separates titanium quantitatively from a large number of the elements commonly occurring with it in ores, notably aluminum.

A procedure for the separation and determination of small amounts of zirconium from large amounts of titanium has been described.

NEW YORK CITY

NOTE

A Neutral Buffered Standard for Hydrogen Ion Work and Accurate Titrations Which Can be Prepared in One Minute

BY ROGER J. WILLIAMS AND CARL M. LYMAN

Most of the standard buffer solutions recommended in the literature must be prepared with considerable care and one cannot be sure of the result unless all the precautions of quantitative analysis are used. A simply prepared solution that can be relied on for standardizing quinhydrone electrodes, etc., is therefore much to be desired. Standardized buffer mixtures are on the market for this purpose.

Ammonium acetate solution has for a number of years been used by one of us in lecture demonstrations of buffer activity, for which purpose