

titration, as the steel contained only about 0.1 per cent. of silicon. But it seems improbable that higher silicon would seriously affect the results from the following considerations. In the first place no especial effort is made to dehydrate the silicic acid nor to prevent its passing directly into the filtrate. Secondly, of the silica remaining with the WO_3 only a small quantity is likely to be dissolved by N/5, potassium hydroxide, and that which is dissolved, the hydrolysis of potassium silicate being very high, would hardly be able to displace the end point far in titrating back with acid.

It is our opinion that the foregoing procedure might be used to good advantage, in laboratories where a large number of tungsten determinations are continually made, but that for occasional determination, the labor of preparing the normal solutions, and in becoming acquainted with the method would perhaps not justify its preference to the gravimetric methods.

It gives us pleasure to express our indebtedness to Prof. E. D. Campbell for his interest and helpful suggestions in this work.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE COLORIMETRIC DETERMINATION OF TITANIUM.

BY JAMES H. WALTON, JR.
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Several investigators have shown¹ that in an alkaline solution which contains an excess of hydrogen peroxide titanium is not precipitated, but remains in solution. It occurred to the writer that this soluble compound of titanium might be formed by heating substances containing titanium with sodium peroxide.

In order to test this idea, about one gram of pure, dry titanium dioxide was intimately mixed with five grams of sodium peroxide in an iron crucible. The two substances had scarcely been mixed, when, without any application of heat, they began to react with each other forming little fused lumps and evolving considerable heat. On dissolving the fusion in water, filtering, and acidifying with sulphuric acid, it was evident from the reddish color of the solution that a considerable portion of the titanium dioxide had been changed to the soluble form. It was necessary to heat to the fusing point in order to bring all of the titanium into solution in this way. A sample of titanium iron ore was completely decomposed by fusion with sodium peroxide. On dissolving the fusion in water, filtering and acidifying, the usual test for titanium was obtained.

Several experiments were also carried out in which the titanium diox-

¹Classen, Ber. 21, 370 (1888); Walker, this Journal 20, 513 (1898).

ide was heated with potassium persulphate and also with the percarbonate. By heating with these substances, however, it was found impossible to form the compound of titanium which is soluble in alkaline solution.

The above method of fusion with sodium peroxide gives a simple and rapid method for the detection of titanium in ores, fire clay, etc. The following procedure should be followed: Heat a few tenths of a gram of the substance in an iron crucible with four to five grams of sodium peroxide. As soon as the mixture has completely melted, cool the crucible and place it in a beaker containing about 300 cc. of *cold* water. Filter and test the filtrate by acidifying with sulphuric acid. In dissolving the fused mass care should be taken that the solution does not get too hot as this breaks up the titanium compound and it precipitates with the iron. The presence of the iron makes the filtration necessary, as the solution would otherwise be colored by ferric sulphate when it was made acid.

The rapidity and completeness of the decomposition of clays, ores, and glazes by fusion with sodium peroxide has suggested its use in the quantitative estimation of titanium. The fusion may be carried out in nickel or silver crucibles. For the gravimetric determination of titanium silver crucibles should be used.

Porcelain crucibles which are sometimes used for sodium peroxide fusions cannot be used, because they often contain small amounts of titanium.

THE QUANTITATIVE DETERMINATION OF SMALL QUANTITIES OF TITANIUM.

The well-known colorimetric method has the disadvantage that in the analysis of substances which contain large amounts of iron the solution is colored by the ferric salts present as well as by the titanium. Moreover, difficulty is often experienced in the decomposition of certain refractory substances with the usual fluxes employed, a long fusion often being necessary.

It was considered possible to overcome these difficulties by using sodium peroxide as a flux. The most refractory ores may easily be decomposed by fusing for less than ten minutes; moreover, the titanium forms a soluble compound, which, it was thought, could be separated from the iron by filtration.

In order to test the separation of titanium and iron in this way, the determination of titanium in a clay was undertaken. This was first analyzed by fusing with potassium acid sulphate, dissolving the fused mass in dilute sulphuric acid, adding hydrogen peroxide, and comparing the color of the solution with that of a standard titanium solution¹. It was found to

¹ Lord, Notes on Metallurgical Analysis, 141.

contain 1.13% TiO_2 . Only a small amount of iron was present in the clay, but enough iron was furnished by the crucible in which the sodium peroxide fusion took place to show the value of this method as a means of separation of titanium and iron.

About one gram of the clay was mixed with eight grams of sodium peroxide and heated in an iron crucible over the flame of an ordinary gas burner. When the mixture had completely fused it was cooled, and to the fused mass 200 cc. of water were added. The solution was made up to a volume of 250 cc., allowed to settle, and the supernatant liquid was decanted through a filter. 100 cc. of the filtrate were acidified with a measured volume of sulphuric acid. No hydrogen peroxide was added as enough was formed by the action of the sulphuric acid on the excess of sodium peroxide present. The color was compared with that of a standard titanium solution.

The results obtained in a number of analyses carried out as above were all lower than those obtained by the acid sulphate fusion method. It was found that a part of the titanium remained behind with the ferric hydroxide precipitate. This amount evidently depends upon several factors, the most important of which are the amount of iron present, the temperature to which the solution rises on dissolving the fused mass, and the quantity of sodium peroxide used. Experiments carried out to diminish the effects of these factors by varying the reagents, temperatures, etc., were successful to an inappreciable extent only.

In the determination of titanium in the presence of iron two methods have been suggested by which the error caused by the color of the ferric sulphate may be avoided. The method of W. A. Noyes¹ consists in adding to the standard an amount of iron equal to that in the solution analyzed. Treadwell² suggests that the color due to ferric sulphate may be removed by the addition of phosphoric acid to the solution, decolorizing the iron as in the determination of iron by the Zimmermann-Reinhardt method.

An experiment was made in which this latter method was used. A sample of clay was fused in an iron crucible as before. This clay contained only a small amount of iron, but in each fusion about 0.2 g. iron was furnished by the action of the sodium peroxide on the crucible. The color of the amount of ferric sulphate thus formed is deep enough to introduce an appreciable error into the determination³. The fusion was dissolved in 200 cc. of water, and without filtering, 15 cc. of sulphuric acid (sp. gr. 1.4) and 6 cc. of 50 per cent. phosphoric acid were added, and the solution made up to 250 cc. On comparing the color of this solution with that of the standard results were obtained, which were lower than those

¹ Noyes, W. A., *Jour. Anal. and Appl. Chem.*, 5, 39.

² Treadwell, *Quantitative Analysis*, Hall's translation, 89.

³ Hillebrand, *Bull. of U. S. Geol. Survey No. 176*, 69.

obtained by the acid sulphate fusion method. In the case of a clay which contained 1 per cent. of TiO_2 the results obtained were from 0.2 to 0.3 per cent. too low. On making a qualitative test it was found that the addition of phosphoric acid diminishes the depth of the yellow color of the titanium solution. To eliminate this error it was only necessary to add to the standard an amount of phosphoric acid equal to that added to the solution analyzed. Using this modification of the method the following substances were analyzed with the accompanying results.

Substance analyzed.	Per cent. Fe Present.	Per cent. TiO_2 obtained by fusion with Acid Sulphate.	Per cent. TiO_2 obtained by fusion with Na_2O_2 and addition of H_3PO_4 to the solution.
Clay	4.3	1.13	1.13
Fireclay	2.7	1.30	1.26
Limestone	1.2	.22	.23
Iron ore	30.	3.73	3.66

The results obtained by using this method are accurate, and the method is satisfactory from the standpoint of rapidity. The presence of sodium peroxide from the fusion makes unnecessary the addition of hydrogen peroxide, as this substance is formed upon acidifying the solution. Upon standing, the yellow color fades. This is probably due to the ferric sulphate present. It has been observed by the writer that in the presence of ferric salts the yellow color of the titanium disappears much more rapidly than in titanium solutions which contain no iron. With substances which contain a large amount of iron the amount of phosphoric acid added should be increased.

A standard solution of titanium is easily prepared by fusing pure titanium dioxide with sodium peroxide, dissolving the fusion in water and adding enough sulphuric acid for the solution to contain 5 per cent. of acid.

THE EFFECTS OF THE PRESENCE OF VARIOUS IMPURITIES ON THE COLOR OF THE TITANIUM SOLUTION.

It has been shown¹ that the presence of hydrofluoric acid and certain other substances diminishes the depth of the yellow color of titanium solutions. Some idea of the amount of the error in the determination of titanium caused by the presence of very small amounts of hydrofluoric acid may be gained from the results of the following experiments.

Pure potassium fluoride was prepared by adding to pure potassium carbonate an excess of hydrofluoric acid, evaporating to dryness, and igniting at a red heat². A solution of potassium fluoride was made and kept in a flask, the inside of which was covered with paraffin to prevent any action of the solution on the glass. Solutions containing equal amounts of titanium, hydrogen peroxide, and sulphuric acid, but with varying amounts of

¹Jackson, Chem. News, 47, 157 (1883); Levy, Compt. rend., 105, 754 (1888) Hillebrand, this Journal, 17, 718 (1895); Reichert, Chem. Ztg., 28, 16 (1904).

²Dammer, Handbuch der Anorganischen Chemie, II, 2, p. 46.

potassium fluoride were compared with a standard solution of titanium in the colorimeter. The following results were obtained:

	Volume of solution c.c.	TiO ₂ present gms.	HFl present gms.	Colorimeter reading obtained by comparing solution with (1) as standard.
1	250	0.010	0.000	100.0
2	250	0.010	0.00039	93.3
3	250	0.010	0.00194	80.2
4	250	0.010	0.0039	67.6

Similarly, the change in color caused by adding different amounts of phosphoric acid to a titanium solution of the same concentration was determined. The phosphoric acid used was prepared by Kahlbaum. The titanium solution contained 5 per cent. sulphuric acid and 2 cc. of 3 per cent. hydrogen peroxide in every 250 cc.

	Volume of solution c.c.	TiO ₂ present gms.	P ₂ O ₅ present gms.	Colorimeter reading obtained by comparing solution with (1) as standard.
1	250	0.010	0.00	100.
2	250	0.010	0.13	90.
3	250	0.010	0.26	83.
4	250	0.010	0.52	74.
5	250	0.010	0.78	69.
6	250	0.010	1.04	66.
7	250	0.010	1.30	64.

That the change in color was not due to an impurity in the phosphoric acid used was proved by the fact that on repeating the experiment with solution (3) and using in 250 cc. of solution 0.638 g. of pure K₂HPO₄ (containing 0.26 g. P₂O₅) instead of phosphoric acid a reading of 82.5 was obtained, which agrees with the value obtained when phosphoric acid was used. Moreover, an experiment in which phosphoric acid obtained from another source was used gave results agreeing with the above.

The influence of the phosphoric acid on the titanium color is of importance in the colorimetric determination of titanium in substances containing any considerable amount of phosphates. The results obtained will be low unless enough phosphoric acid is added to the standard to compensate the effect of that in the sample.

A STUDY OF THE ATOMIC WEIGHT OF INDIUM.¹

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Historical.

The first determinations of the atomic weight of indium were made by Reich and Richter², who obtained values that varied from 110 to 112.

¹NOTE.—The following investigation by Mr. Mathers upon the Atomic Weight of Indium is a continuation of the work that was first taken up in the Cornell Laboratory by Mr. W. C. Geer.

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²Reich and Richter, J. pr. Chem., 92, 480 (1864).