It is a pleasure to express my gratitude to Professor M. A. Rosanoff for a number of helpful suggestions in connection with this work. Indirectly my thanks are also due to the National Academy of Sciences, for the use of instruments placed at the disposal of Professor Rosanoff and his students by the Committee of the Bache Fund.

WORCESTER, MASS.

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

THE VOLUMETRIC ESTIMATION OF TITANIUM BY MEANS OF FERRIC CHLORIDE.

BY T. R. BALL AND G. McP. SMITH.

Received June 30, 1914.

The tedious operations involved in the quantitative separation of titanium from iron, aluminium, etc., render it desirable to find a convenient and reliable volumetric process for the direct determination of this element in the presence of the above mentioned substances.

With this end in view, various processes have been proposed for the volumetric estimation of titanium. All of these are based upon the fact that titanic salts are under certain conditions capable of being reduced quantitatively to salts of trivalent titanium, which, in turn, may readily be oxidized back to the tetravalent condition; as oxidizing agents for this purpose have been proposed, potassium permanganate, methylene blue, and ferric salts.

Owing to the difficulty experienced in titrating with permanganate in the presence of ferrous iron and hydrochloric acid, Wells and Mitchell[1] reduce the iron in sulfuric acid solution with hydrogen sulfide, and then titrate the iron alone with potassium permanganate. In the resulting solution they reduce the iron and the titanium with zinc, after which both metals are titrated with potassium permanganate. The titanium is, of course, gotten by difference. According to the authors, the results are always somewhat low.

In accordance with Wells and Mitchell, Newton[2] reduces the two metals in sulfuric acid solution with zinc, in an atmosphere of hydrogen. Then, however, in order to lessen as much as possible the oxidizing action of air on the solution during the subsequent operations, he adds an excess of ferric sulfate solution. In this way, the titanous sulfate present is at once oxidized at the expense of an equivalent quantity of the ferric iron, and the total ferrous iron in the resulting solution is titrated with potassium permanganate.[3]

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[1] THIS JOURNAL, 17, 878 (1895).

[2] *Am. J. Sci.*, 25, 130 (1908).

[3] According to either of these methods, it is necessary to correct for any iron which may be contained in the zinc. No such correction has to be made in the case of the methylene blue and ferric salt titration methods.

Neumann and Murphy[1] have recently investigated the use of methylene blue as an oxidizing agent for the direct titration of trivalent titanium in the presence of ferrous salts. In this case the methylene blue is decolorized and is therefore its own indicator. While the results obtained are very exact, the end point of the titration is rather slowly attained and is recognized best in a solution heated nearly to boiling, whose volume is about 150 cc., and to which a very considerable proportion of concentrated hydrochloric acid has been added. Furthermore, the standard solution of methylene blue does not retain its strength; it must occasionally be standardized against known quantities of freshly reduced titanium, and this also detracts somewhat from the convenience of the method.

E. Knecht, who first made use of titanous salts as reducing agents in organic chemistry,[2] has studied their action also upon certain inorganic salts. Knecht and Hibbert[3] have recommended the use of titanous chloride solutions for the volumetric estimation of ferric iron. The reaction is indicated by the equation:

$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4$$

With potassium thiocyanate as an indicator, they were able to obtain very satisfactory results for iron, and their method has been found by others to give very exact results. In his original publication Knecht gives a single, somewhat low, result obtained by employing the reaction for the estimation of titanium.[4]

F. W. Hinrichsen[5] later determined titanium by means of ferric iron with results which he does not give, but which he says are satisfactory. As the reducing agent he recommends a 50% zinc-magnesium alloy in hydrochloric acid.

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[1] *Z. angew. Chem.*, 26, 613 (1913). Neumann and Murphy in their paper state the reaction to be that expressed by the "equation:"

$$C_{16}H_{18}N_3SCl + 2TiCl_3 + HCl = C_{16}H_{18}N_3S + 2TiCl_4.$$

The following equation is probably correct:

$$C_{16}H_{18}N_3SCl + 2TiCl_3 + 2HCl = C_{16}H_{20}N_3SCl + 2TiCl_4.$$

[2] *Ber.*, 36, 166 (1903). The methylene blue reaction given above was discovered by Knecht.

[3] *Ber.*, 36, 1549 (1903).

[4] Neumann and Murphy, *loc. cit.*, claim that the degree of accuracy attainable by the methylene blue method is greater than that to be had by any other method for the determination of titanium, and that it is the only method which permits of the direct estimation of titanium in the presence of iron, silica, alumina, etc. While they mention the ferric salt method, they erroneously state that it can be used only in connection with "Rothe's ether method." These statements are justly criticized by Knecht (*Z. angew. Chem.*, 26, 734 (1913)), but Knecht refers only to the work of Hinrichsen, without giving any additional data. In the determination of titanium by any of these volumetric methods, substances such as tin, chromium, vanadium, tungsten and molybdenum must of course be absent.

[5] *Chem. Ztg.*, 31, 738 (1907).

G. Gallo[1] has also investigated the same method. He recommends that the reduction be carried out with zinc at 10° in rather strong sulfuric acid. His results are very good, but he allows 12 hours for the complete reduction of the titanium.

In view of the ease with which standard ferric salt solutions may be prepared and kept, as compared with those of titanous salts (which have to be preserved under carbon dioxide or some other inert gas, and which even then require frequent standardization), it seems strange that Knecht and Hibbert did not place especial emphasis upon the use of the above reaction for the determination of titanium, rather than for that of ferric iron.

Experimental.

Standard Titanium Sulfate Solution.—Exactly 6 g. of pure K_2TiF_6[2] were twice evaporated with sulfuric acid. The residue from the second evaporation was treated with a few cc. of sulfuric acid, and the mixture was then taken up with 5% sulfuric acid, of which a sufficient quantity was finally added to make the volume up to 1 liter.

The ignited precipitate obtained upon neutralizing 50 cc. of this solution with ammonia, adding acetic acid and sodium acetate, and boiling for several minutes, weighed 0.1002 g. (calculated weight = 0.1000 g. TiO_2).

A second, less concentrated, solution was prepared by making 100 cc. of the standard solution up to 1 liter with 5% sulfuric acid.

Standard Ferric Chloride Solution.—Pure ferric chloride was dissolved in water with the addition of enough hydrochloric acid to give a perfectly clear solution. The resulting solution was standardized by running 30 cc. portions of it from a buret, with stirring, into an excess of aqueous ammonia; in each case the precipitate was filtered off and ignited to constant weight. Two such determinations gave as normality factors 0.05043 and 0.05041; the mean of these was taken as correct.

A less concentrated solution was prepared by diluting 100 cc. of the standard solution to a volume of 500 cc. The normality of this solution was taken to be 0.05042 ÷ 5 = 0.010084.

The indicator was a saturated solution of potassium thiocyanate, of which 1 cc. was used in each titration.

Zinc was found to be a satisfactory reducing agent. Several other metals were tried.

In all cases the titanous solution should be carefully guarded from oxidation by air after the reduction and during titration. In the determinations to be given below the solution was in most cases protected by an

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[1] *Atti Roy. Acad. d Lincei,* [5] 16, I, 325–30; *Chem. Zentrlb.*, 1907, p. 1600.

[2] This salt was prepared by crystallizing three times in platinum pure $K_2TiF_6.H_2O$ from dilute hydrofluoric acid; the dried product was finally ignited in platinum.

ordinary Contat-Gockel valve. This does very well if the solution is reduced in the cold, but with hot solutions the slightest cooling causes sodium bicarbonate solution from the valve to enter the reduction flask. While small quantities of sodium bicarbonate do no harm, larger quantities use up much of the acid and it might therefore be desirable to prevent this feature altogether. This may be accomplished by means of the modified valve shown in Fig. 1.

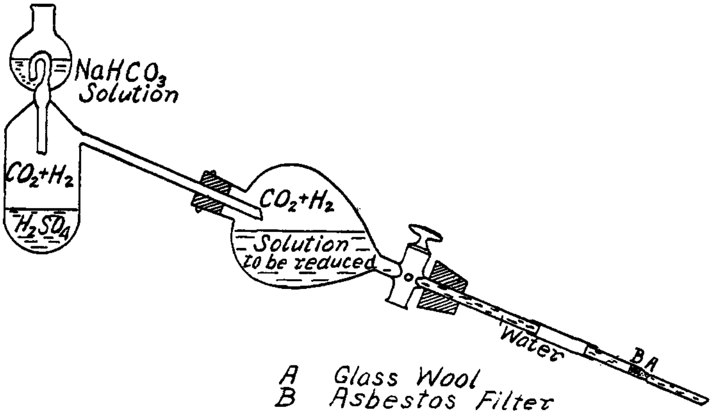

Fig. 1.

In carrying out the reduction with zinc, it is not always practicable to completely dissolve the metal, and sometimes it is almost impossible to do so. The solution must be filtered therefore before titration from the unused zinc, even when sheet or bar zinc is used. Since the reduction can be carried out at room temperature, separatory funnels of 250 cc. capacity are recommended as containing vessels. A glass tube of the same diameter as the funnel stem and about 4 inches in length is drawn out from its middle point, and upon the resulting constriction a small mat of glass-wool and asbestos is placed, to serve as a filter. A rubber (suction-flask) stopper is fitted upon the stem of the funnel, and the filter tube is then attached to the stem by means of rubber tubing. Before beginning a reduction, the funnel stem and filter tube are filled with freshly boiled water, after which the strongly acid solution and a large excess of zinc are introduced into the funnel; the air is displaced from the latter by carbon dioxide from a generator, and the mouth of the funnel is then fitted with a Contat-Gockel valve.[1] The reduction is allowed to proceed for about 2 hrs., after which the valve is removed and the solution is drawn through the filter into a suction flask previously filled with carbon dioxide, the funnel being washed out with freshly boiled water in such manner

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[1] If the modified valve shown in the figure is used, it should be filled with carbon dioxide just before being connected with the funnel.

as not to permit the entrance of any air into the funnel tube; the end of the filter tube should reach to the bottom of the suction flask. After the addition of the indicator, the reduced solution is rapidly titrated with standard ferric chloride solution.[1]

The apparatus used for carrying out the reduction is illustrated in Fig. 1, in which the modified valve referred to above is shown, instead of the ordinary Contat-Gockel valve.

The results obtained with the above solutions are given in Table I.

TABLE I.[2]

No.	TiO_2 taken, g.	TiO_2 found, g.	Fe_2O_3 present before reduction, g.	Acid used.	Temperature of reduction.	Form of zinc.
1	0.0600	0.0601	None	10 cc. HCl (sp. gr. 1.19)	Boiling	Bar
2	0.0390	0.0389	None	10 cc. HCl (sp. gr. 1.19)	Room	Granulated[3]
3	0.0500	0.0503	None	10 cc. H_2SO_4 (1 : 1)	Boiling	Granulated
4	0.0500	(0.0486)	None	10 cc. H_2SO_4 (1 : 1)	Boiling	Granulated
5	0.0500	0.0503	None	10 cc. H_2SO_4 (1 : 1)	Room	Granulated
6	0.0500	0.0504	None	10 cc. H_2SO_4 (1 : 1)	Room	Granulated
7	0.0200	0.0202	None	10 cc. H_2SO_4 (1 : 1)	Room	Bar
8	0.0020	0.0020	0.1000	10 cc. H_2SO_4 (1 : 1)	Room	Granulated
9	0.0100	0.0097	0.1328	10 cc. H_2SO_4 (1 : 1)	Room	Granulated
10	0.0100	0.0097	0.1328	10 cc. H_2SO_4 (1 : 1)	Room	Granulated
11	0.0200	0.0200	0.1328	10 cc. H_2SO_4 (1 : 1)	Room	Granulated
12	0.0200	0.0199	0.1328	10 cc. H_2SO_4 (1 : 1)	Room	Granulated

A sample of ilmenite, in which, by means of duplicate analyses according to the Gooch gravimetric method, 34.60% and 34.65% of TiO_2 were found, was also analyzed by the ferric chloride method.

It is very difficult by means of the usual pyrosulfate fusion method to get into solution substances such as ilmenite and other titaniferous iron

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[1] It might be well, before beginning a reduction, to place upon the asbestos filter a little granulated zinc, and upon removing the valve at the end of the reduction to introduce into the mouth of the funnel the open outlet-tube of a carbon dioxide generator; furthermore, it would do no harm to pass carbon dioxide through the suction flask during the titration. These precautions were, however, omitted in the above work, and the results are nevertheless good.

[2] All of the above titrations were made in the cold, after having filtered the solution from undissolved zinc into an atmosphere of carbon dioxide. In the determinations in which the reduction was carried out at the boiling temperature, the solutions were allowed to cool to room temperature before they were filtered off and titrated.

Determination No. 8 was carried out with 0.010084 *N* $FeCl_3$ and the result shows that, by using 0.01 *N* $FeCl_3$ solution, as small a quantity of TiO_2 as 0.002 g. may be accurately determined in the presence of a large excess of iron. It might, however, be preferable to use the Weller colorimetric method in the case of such small quantities of titanium. All of the other titrations were performed with 0.05042 *N* $FeCl_3$ solution.

[3] The granulated zinc referred to was 20–30 mesh, "C. P." and was used without amalgamation or further treatment.

ores. E. Knecht[1] fuses 0.5–1.0 g. of the mineral (*e. g.*, rutile) for 10 minutes with 10 parts by weight of potassium hydroxide, after which he washes the mass into a beaker containing a large excess of hydrochloric acid.

A method far better suited to our purpose was suggested to us by Professor W. A. Noyes.[2] According to this, the finely powdered ore is mixed with 1 part, by weight, of potassium fluoride and 5 or 6 parts of potassium pyrosulfate and fused in a platinum crucible for 15–20 minutes, until effervescence ceases. The cooled mass is then readily dissolved by hydrochloric acid to a clear solution which is ready for reduction.

With solutions prepared in this way, the ferric chloride volumetric method gave the following independent values: 34.63, 34.47, 34.44, and 34.42% of TiO_2 (mean value = 34.49%). The reduction in this case also requires not more than two hours.[3]

The ferric chloride method is thus seen to compare very favorably with the tedious gravimetric method of Gooch, and it is incomparably shorter. Such metals as tin, chromium, vanadium, tungsten, and molybdenum must, however, be absent when the solution is reduced with zinc.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OREGON AGRICULTURAL EXPERIMENT STATION.]

THE ARSENATES OF LEAD.[4]

BY HERMAN V. TARTAR AND R. H. ROBINSON.

Received June 17, 1914.

Introduction.

Some of the arsenates of lead are widely used at present as stomachic insecticides. The general properties of these compounds seem to specially adapt them for this purpose and for this reason they have been used more extensively in recent years than any other arsenical. In response to the demand for these materials, their commercial manufacture has now reached large proportions and a number of manufacturing chemists in the United States are making them in considerable quantity. This extended use of certain of the arsenates of lead for insecticidal purposes

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[1] *Z. angew. Chem.*, **26**, 734–5 (1913). Knecht dilutes the HCl solution to 250 cc. and reduces a 25 cc. portion of it with granulated zinc and hydrochloric acid for 10–20 minutes, until the zinc is completely dissolved. He then suspends a zinc rod in the hot solution by means of a platinum wire which is passed through the Bunsen valve, and allows the solution to cool; finally he passes in carbon dioxide and titrates with ferric alum.

[2] *J. Anal. Appl. Chem.*, **5**, 39 (1891).

[3] Since in all cases good results were obtained after 2 hours' reduction, that time is to be considered sufficient. While in some cases less time might suffice, it is safer always to allow at least 2 hours for the reduction.

[4] Presented at the Cincinnati meeting of the American Chemical Society, April, 1914.