

# A RAPID VOLUMETRIC METHOD FOR ESTIMATION OF IRON AND TITANIUM AND ITS APPLICATION TO ILMENITE ANALYSIS

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DURING recent years the production of ilmenite has increased steadily owing to the progress of the titanium oxide paint industry. Several scores of samples of the mineral had to be analysed by us in rapid succession in these laboratories and difficulties were experienced in the course of the work as the standard methods given in chemical literature were tedious and inconvenient.

The well-known colorimetric method for titanium which has been fully investigated by Hillebrand (1895), Walton, Jr. (1907), Faber (1907), Merwin (1909) and Wells (1911) can be usefully employed only when small amounts of titanium are present.

The gravimetric methods for estimation of titanium involve several precautions especially when iron also is present. Gooch (1885), Barnaby and Isham (1910), Thornton (1914), Lundell and Knowles (1919) and Hillebrand (1919) and others have devised various procedures, but all of them call for careful control of several factors and are therefore inconvenient.

Several volumetric methods for estimation of titanium have been suggested from time to time, the more important of them being due to the following investigators: Pisani (1864) Knecht and Hibbert (1903), Knecht (1905), Gallo (1907), Newton (1908), Eva Hibbert (1909), Shimer and Shimer (1912), Newmann and Murphy (1913), Ball and Smith (1914), Lundell and Knowles (1923), Takeno (1934), Thornton and Roseman (1935) and Hope Morgan and Ploetz (1936). The methods suggested by the above-mentioned workers utilise simple methods of reduction of the titanium followed by an oxidimetric titration with permanganate, ferric alum or other reagents. These will be referred to later in this paper.

The procedure for volumetric estimation of iron in presence of titanium usually consists in reduction with hydrogen sulphide and subsequent titration with permanganate. The method has been very carefully studied by Wells and Mitchell (1895), Coppadoro (1901), Washington (1904), McBride and Scherrer (1917), Hillebrand (1919) and Lundell and Knowles (1921). All

workers lay stress on the importance of observing several precautions if accurate results are desired and these will be referred to in detail, later in this paper.

### *Experimental*

*Preparation of Solutions and their Standardisation.*—0.1 N solution of potassium permanganate was prepared in the usual way and was accurately standardised by titration with pure sodium oxalate.

Approximately 0.05 N solution of ferric ammonium sulphate was prepared by weighing out the calculated amount of ferrous ammonium sulphate of known purity (99.51%) dissolving it in water containing a small quantity of sulphuric acid and then oxidising it completely by heating with the minimum quantity of nitric acid. The solution was boiled to free it from oxides of nitrogen and then made up to volume after cooling. This solution was standardised by different methods as described below.

Titanium solution containing approximately 4 mg. per c.c. was prepared by fusing several portions of 5 g. of carefully purified  $TiO_2$  with pure potassium bisulphate in hard glass test-tubes and dissolving the melt in dilute sulphuric acid and diluting the solution to the required volume. A saturated solution of potassium thiocyanate was employed in the titration of titanous salt with standard ferric salt solution.

Reduction of solutions was carried out in a Jones reductor which was of the usual size and contained a column of zinc about 35 cm. long resting on glass beads and glass wool. To prevent oxidation, the flask for receiving the reduced solutions was provided with inlet and outlet tubes for carbon dioxide.

The standardisation of the ferric salt solution was carried out by titration with standard permanganate after the solution had been reduced by either (a) hydrogen sulphide or (b) zinc in the reductor, observing the necessary precautions. Six experiments by each of the two methods gave the mean values 4.153 and 4.159 respectively, the general mean of all the experiments being 4.156 mg.  $Fe_2O_3$  per c.c. of the ferric salt solution.

The titanium solution was standardised by the following methods: In one set of experiments, 25 c.c. portions of the titanium solution were reduced in the Jones reductor and the reduced solution collected in an excess of ferric salt solution, a supply of carbon dioxide to the receiving flask being maintained throughout the experiment. The solution in the receiving flask was then immediately titrated with standard permanganate. It is well known that this procedure yields accurate results (Shimer and Shimer, 1912), owing to

the fact that titanous salt which is very unstable gets oxidised immediately by the ferric salt present, yielding an exactly equivalent amount of the relatively stable ferrous ion which can be titrated with better results. The titanium solution was also standardised after reduction, by titrating it with standard ferric solution, employing potassium thiocyanate as internal indicator. This titration had to be carried out quickly as otherwise low values were obtained owing to the rapid oxidation on exposure to air. A modification of this procedure which we devised was to keep in the vessel receiving the reduced solution, almost the required quantity of standard ferric solution as was known from the preliminary titrations. Usually 0.2–0.3 c.c. less than the quantity required was delivered from the burette into the receiving flask in which the reduced solution was to be collected, the reduced solution was then collected in it and the titration completed by cautious addition of ferric solution from the same burette after adding a small quantity of thiocyanate solution. We obtained very consistent results by this procedure and this involved no inconvenience or extra time.

The titanium solution was also standardised gravimetrically by precipitation with (a) ammonium hydroxide and (b) with sulphur dioxide. Six determinations were made by each of the two methods. The results obtained were in good concordance but the mean value obtained gravimetrically was higher by 0.18% than that obtained from the volumetric estimations.

*Estimation of Iron in presence of Titanium.*—One of the oldest methods for the estimation of iron in presence of titanium consists in passing hydrogen sulphide into the solution containing the two metals whereby only the iron is reduced while the titanium remains unaffected, thereby enabling the determination of the ferrous iron by titration with standard permanganate. The method is somewhat tedious and yields erratic results unless several conditions are strictly adhered to.

We carried out several experiments under varying conditions to investigate the reliability of the hydrogen sulphide reduction method for estimating iron, both in the presence and in the absence of titanium, the procedure being as follows: 25 c.c. of standard ferric solution was taken either by itself or along with 25 c.c. of standard titanium solution as required and diluted with water to about 200 c.c. Known quantities of sulphuric acid ranging from 2 to 20 c.c. were added, the solution heated almost to boiling and a steady current of purified hydrogen sulphide was passed for periods ranging from 1 to 3 hours. The current of hydrogen sulphide was maintained until the solution cooled to room temperature after which a current of purified

carbon dioxide was led into the solution which was gradually heated up to the boiling point. The heating was stopped as soon as the escaping vapours gave no test for hydrogen sulphide, and the solution was allowed to cool, the current of carbon dioxide being maintained throughout. The cooled solution was then titrated with standard permanganate solution. The results obtained are given in Table I, each value being the mean of at least six different experiments. The figures under col. A refer to the experiments where the solutions contained only iron and those under col. B to the solutions containing both iron and titanium. The results given in Table I show clearly that satisfactory results can be obtained by this method whether in the presence or in the absence of titanium, only if the acid concentration is maintained below about 3%.

TABLE I  
*Estimation of Iron by Reductions with H<sub>2</sub>S*

Concentration of	Period	KMnO <sub>4</sub> required	
		A c.c.	B c.c.
H <sub>2</sub> SO <sub>4</sub> %	hrs.		
2.0	1	13.02	13.00
3.1	1	13.00	13.02
4.0	1	12.95	12.94
5.0	1	12.90	12.90
5.0	3	12.80	12.85
10.2	1	12.45	12.60
10.2	3	12.32	12.40

The volumetric estimation of iron by reduction of the solution with zinc and subsequent titration with standard permanganate was modified in the following manner, when titanium was also present in the solution. Since titanium is quantitatively reduced to the trivalent state in the reductor, while iron is being quantitatively reduced to the bivalent condition, treatment of the reduced solution with permanganate will yield a titration value corresponding to the sum of iron and titanium present. Since, however, titanous salts undergo rapid oxidation in air before titration is completed, it is necessary to collect the reduced solution from the reductor in an excess of ferric salt solution and thereby generate an equivalent amount of ferrous iron which

can be titrated with better results as it is relatively stable. Therefore, under the conditions of this experiment, the permanganate consumption represents the iron originally present in the solution as well as a quantity of iron exactly equivalent to the titanium present. The iron content of the original solution can therefore be calculated from this titration value by deducting the iron equivalent of the titanium which is determined by the method indicated below.

*Estimation of Titanium in presence of Iron.*—The most satisfactory procedure for the estimation of titanium whether in presence or absence of iron consists (as has been indicated earlier) in the reduction of the solution with zinc in the reductor and its subsequent titration with ferric salt solution. A useful modification which we devised was to collect the reduced solution in slightly less (0.2–0.5 c.c.) than the required quantity of ferric salt solution (as known from a preliminary experiment) and completing the titration in the usual manner, employing thiocyanate as indicator. We found that a sharp end point was obtained if 4 to 5 drops of the indicator were added and that it was unnecessary to use 5 c.c. of it as suggested by several workers.

*Estimation of Titanium and Iron when both Metals are present.*—The preliminary studies outlined above enabled us to adopt the following procedure for carrying out estimations of titanium and iron when both metals were present. 25 c.c. portions of standard iron solution were mixed with 25 c.c. portions of standard titanium solution, 10 c.c. of sulphuric acid (1 : 1) was added to the mixture which was then diluted to about 100 c.c. and used in each of the following experiments. The mixed solution was reduced in the reductor and titrated immediately with standard ferric solution and the quantity of ferric solution required was noted. Since this value was always low (as pointed out earlier) a fresh portion of the mixed solution was reduced in the reductor and the reduced solution caught in standard ferric solution (0.2–0.3 c.c. less than the quantity required in the previous experiment) and the titration completed as usual by further addition of standard ferric solution from the same burette. This modified procedure gave consistently accurate values for the titanium content of the solution, whereas the values calculated from the first experiment were too low as illustrated in the following example. In the first experiment, the mixed solution containing 25 c.c. of standard titanium solution (0.09820 g.  $\text{TiO}_2$ ) required after reduction 23.45 c.c. of standard ferric solution, which corresponded to 0.09769 g.  $\text{TiO}_2$ . In the second set of experiments where 23.25 c.c. of standard ferric solution was kept in the receiving flask to collect the reduced solution and the titration completed with additions from the burette, the total quantity

required was 23.55 c.c. which corresponded to 0.09811 g.  $\text{TiO}_2$  which is very close to the true value.

The estimation of iron in the solution containing both iron and titanium was carried out by titration with permanganate as follows. Since both iron and titanium are reduced quantitatively to the bivalent and trivalent stages respectively by zinc in the reductor, a titration of the reduced solution with permanganate will involve a permanganate consumption corresponding to the total of the iron and titanium present. As the quantity of titanium present (or its ferrous oxide equivalent) in the solution has been determined by previous titration with standard ferric solution, the corresponding permanganate consumption is also known. The quantity of permanganate required to oxidise only the ferrous iron is readily ascertained and the iron content of the solution calculated as usual. Since titanous solutions get readily oxidised in contact with air we adopted the procedure of collecting the reduced solution in an excess of ferric salt solution with the result that a quantity of ferrous iron exactly equivalent to the titanium was formed and which could be titrated with greater certainty. The calculation of results from the titration values may be illustrated by the following example:

(a) The mixture containing 25 c.c. of standard titanium solution (0.09820 g.  $\text{TiO}_2$ ) and 25 c.c. of standard ferric sulphate solution (0.1038 g.  $\text{Fe}_2\text{O}_3$ ) was passed through the reductor and found to require 23.57 c.c. of standard ferric solution. Since 1 c.c. of the standard ferric solution was known to correspond to 4.166 mg. of  $\text{TiO}_2$ , the  $\text{TiO}_2$  content of the solution is found to be 0.0982 g.

(b) The mixture containing 25 c.c. of standard titanium solution and 25 c.c. of standard ferric solution was passed through the reductor and found on titration to require 25.30 c.c. of standard permanganate. Since we know from (a) that 0.0982 g. of  $\text{TiO}_2$  is present and as this would on reduction consume 12.30 c.c. of the same permanganate, we find by subtraction that 13.00 c.c. of permanganate are consumed entirely by the ferrous iron formed from the iron in the solution originally taken for the analysis. Since 1 c.c. of the permanganate solution (0.1001 N) corresponds to 0.007995 g. of  $\text{Fe}_2\text{O}_3$ , we find that the iron content of the solution is 0.1040 g. of  $\text{Fe}_2\text{O}_3$ .

The true values of the iron and titanium contents of the solution taken for analysis are 0.09820g.  $\text{TiO}_2$  and 0.1038g.  $\text{Fe}_2\text{O}_3$  from which it can be seen that the experimental values are accurate. A final series of experiments was conducted with rigorous precautions which included the taking of varying quantities with a weight-burette. The results obtained are given below in Table II. The limits of accuracy obtainable with this method are also given in the table.

TABLE II

*Analysis of Mixtures of Iron and Titanium*

Quantities taken		Quantities found		Error per cent	
Fe <sub>2</sub> O <sub>3</sub> g.	TiO <sub>2</sub> g.	Fe <sub>2</sub> O <sub>3</sub> g.	TiO <sub>2</sub> g.	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
0.0714	0.1246	0.0712	0.1248	-0.27	+0.2
0.0840	0.1108	0.0842	0.1103	+0.25	-0.2
0.0914	0.1012	0.0916	0.1008	+0.22	-0.2
0.0972	0.0988	0.0970	0.0984	-0.21	-0.2
0.1002	0.0890	0.1002	0.0892	0.0	+0.2
0.1014	0.0816	0.1010	0.0816	-0.37	0
0.1102	0.0727	0.1104	0.0724	+0.19	-0.2

It can be seen from the above table that the maximum error in any determination is about 0.4 %, indicating thereby that the procedure adopted is reliable and sufficiently accurate.

*Analysis of Ilmenite*

*Solutions required and their Standardization.*—An approximately 0.1 N solution of potassium permanganate accurately standardised with sodium oxalate. An approximately 0.05 N solution of ferric sulphate is prepared by weighing out the calculated amount of ferrous ammonium sulphate, dissolving the salt in water containing some sulphuric acid, oxidising by warming with a small quantity of nitric acid and making it up to the required volume. 25 c.c. of this solution should give a permanent pink coloration with a drop of 0.1 N potassium permanganate solution.

The ferric solution is standardised by passing 25 c.c. of it through a Jones reductor and titrating the reduced solution with standard potassium permanganate. From this titration, the Fe<sub>2</sub>O<sub>3</sub> value per c.c. of the ferric solution is easily obtained.

The ferric sulphate solution should also be standardised with a solution of known titanium content. The solution of known titanium con-

reduced in the reductor and titrated with the ferric sulphate solution employing thiocyanate as indicator and observing the precautions mentioned earlier in this paper. From this titration we get the direct value per c.c. of the ferric solution in terms of  $\text{TiO}_2$ . In our experiments we found that the  $\text{TiO}_2$  value as obtained by this titration agreed closely with the value calculated from the strength of the ferric solution with reference to permanganate.

The results of standardisation of the solutions employed for this work are given below :

1. The strength of the  $\text{KMnO}_4$  solution was found to be 0.1001 N from which we get by calculation that 1 c.c. of it corresponds to 0.007995 g. of  $\text{Fe}_2\text{O}_3$  or 0.007990 g. of  $\text{TiO}_2$ .

2. (a) 25 c.c. of the ferric sulphate solution required after reduction 13.00 c.c. of  $\text{KMnO}_4$  (0.1001 N). Since 1 c.c. of the  $\text{KMnO}_4$  solution corresponds to 0.007995 g.  $\text{Fe}_2\text{O}_3$  (1), we find that the ferric solution has an  $\text{Fe}_2\text{O}_3$  content of 0.004154 g. per c.c. From this it can also be found that 1 c.c. of the ferric solution will be equivalent to 0.004154 g. of  $\text{TiO}_2$ . (b) 25 c.c. of titanium solution containing 0.0982 g.  $\text{TiO}_2$  required after reduction 23.57 c.c. of ferric sulphate solution. Therefore 1 c.c. of the ferric solution represents 0.004166 g. of  $\text{TiO}_2$ , and this value is in fair agreement with the value calculated in 2 (a).

3. 25 c.c. of titanium solution (0.0982 g.  $\text{TiO}_2$ ) required after reduction 12.30 c.c. of  $\text{KMnO}_4$  (0.1001 N). Hence 1 c.c. of  $\text{KMnO}_4$  corresponds to 0.007984 g.  $\text{TiO}_2$  and this is in good agreement with the value 0.007990 obtained directly by calculation from the strength of the permanganate solution 2 (a).

*Analysis of Ilmenite.*—1.5 g. of the finely crushed sample is fused in a hard glass test-tube with 10–12 g. of potassium bisulphate until decomposition is complete. The fused mass is then digested with sulphuric acid (1 : 4) until extraction of soluble matter is complete. The silica which separates may be filtered off, ignited and weighed if required. Otherwise no filtration is necessary and the entire acid extract may be transferred to a 500 c.c. volumetric flask and diluted with water up to the mark. The concentration of sulphuric acid in the solution could range from 10–15 % without detriment to ease of operation or accuracy of results. 50 c.c. portions of the solution from the volumetric flask are withdrawn for estimations of titanium and 100 c.c. portions for estimations of iron and the determinations carried out by the methods already described in the paper. The calculation of the results of analysis of a sample of ilmenite is illustrated below by an example.



1.2050 g. of ilmenite was fused and brought into solution and made up to 500 c.c.

(a) 50 c.c. of the solution was reduced in the Jones reductor and it was found to require 15.55 c.c. of standard ferric sulphate solution. Since this value is always rather low, the experiment was repeated with the modification that the reduced solution was caught in 15.30 c.c. of the standard ferric solution kept in the receiving flask of the reductor, and the titration completed by additions of ferric solution from the burette. The quantity of ferric solution consumed was 15.62 c.c.

Since we know that 1 c.c. of the ferric solution corresponds to 0.004166 g. of  $\text{TiO}_2$ , it follows that the  $\text{TiO}_2$  in the sample is

$$\frac{15.62 \times 10 \times 0.004166 \times 100}{1.2050} = 54.01 \% \text{TiO}_2.$$

(b) 100 c.c. of the solution was reduced in the reductor and the reduced solution collected in 50 c.c. of ferric sulphate solution. On titration this required 24.30 c.c. of  $\text{KMnO}_4$ .

We know from (a) that 100 c.c. of this solution contains 0.1301 g. of  $\text{TiO}_2$ , and this would after reduction consume 16.30 c.c. of  $\text{KMnO}_4$ , because 1 c.c. of  $\text{KMnO}_4$  corresponds to 0.007984 g.  $\text{TiO}_2$ . Hence 24.30 - 16.30 c.c., viz., 8.00 c.c. of permanganate corresponds to the quantity of iron present. Since 1 c.c. of the permanganate corresponded to 0.007995 g. of  $\text{Fe}_2\text{O}_3$ , the iron content of the specimen is

$$\frac{8 \times 5 \times 0.007995 \times 100}{1.2050} = 26.55 \% \text{Fe}_2\text{O}_3.$$

Since it would be incorrect to express all the iron present in the mineral as  $\text{Fe}_2\text{O}_3$  or as  $\text{FeO}$  unless a separate estimation of  $\text{FeO}$  present in the sample is carried out, it would be advisable to express the iron content in terms of the metal when the result is expressed as  $\text{Fe} = 18.55 \%$ .

In conclusion, we might report that several samples of ilmenite have been analysed by the above procedure both by us and by several other workers in these laboratories with satisfactory results.

#### Summary

1. A rapid volumetric procedure has been devised for the estimation of iron and titanium by titration with solutions of (a) ferric sulphate and (b) potassium permanganate.

2. The application of the above method to the analysis of ilmenite is described.

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