# DIFFERENTIAL IODIMETRY.

## III. DETERMINATION OF THE AVAILABLE OXYGEN IN SOLUBLE AND PRECIPITATED OXIDIZED FORMS OF MANGANESE.

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The reaction in acid solution between an iodide and manganese of a higher valence than two giving a manganese salt and liberating iodine, is well known. Also the reduction of ferric to ferrous iron by iodide has been studied. Both reactions have been used for quantitative purposes and form the bases of reliable methods in common use. When ferric iron and oxidized forms of manganese occur together, the iodide reaction has had no application for the determination of the degree of oxidation of the manganese. Inasmuch as ferric iron contaminates practically all of the commercial manganese products and some of the more purified chemicals to a greater or less extent, this valuable reaction has had no utilization for the evaluation of such products.

Ferric iron in dilute phosphoric acid solution[1] has been shown by one of us to have an inappreciable rate of reaction with iodide at ordinary temperatures. Based on this fact certain quantitative methods have been developed. In this paper are reported the results of a study of the determination of the degree of oxidation of various manganese products in the presence of ferric iron.

A study was made of the titration of an oxidized soluble manganese salt (0.2 $N$ potassium permanganate) in the presence of ferric iron (0.1 $N$ ferric sulfate). The permanganate and ferric sulfate solutions were placed in an Erlenmeyer flask and diluted to 80 cc. 10.0 cc. of $N$ potassium iodide and 10.0 cc. of 2 $N$ phosphoric acid were added, and the solution was shaken and allowed to stand for 3 minutes. The iodine was then titrated with 0.1 $N$ thiosulfate, using starch as indicator (see Table I).

TABLE I.

Titration of Permanganate in the Presence of Ferric Iron.

| Fe$_2$(SO$_4$)$_3$ present (g.). | KMnO$_4$ present (g.). | KMnO$_4$ found (g.). |
|---|---|---|
| 0.0 | 0.0695 | 0.0693 |
| 0.0 | 0.0695 | 0.0695 |
| 0.1 | 0.0695 | 0.0695 |
| 0.2 | 0.0695 | 0.0695 |
| 0.4 | 0.0695 | 0.0695 |
| 0.8 | 0.0695 | 0.0694 |
| 1.2 | 0.0695 | 0.0696 |

The results of Table I show that in the presence of ferric iron, permanganate can be titrated accurately iodimetrically in phosphoric acid solution.

[1] Barnebey, THIS JOURNAL, 37, 1497 (1915); 38, 330 (1916); 39, 604 (1917).

Artificial oxides were investigated to ascertain if conditions similar to the foregoing would cause complete reaction of oxide and iodide.

Various precipitated manganese dioxide products dried at 105° were analyzed by treating the weighed samples with 10 cc. of $N$ iodide and 10 cc. of 2 $N$ phosphoric acid. The solution was agitated gently until the reaction was complete and was then titrated with thiosulfate as before (see Table II). Bunsen's distillation method[1] was used to obtain the results given in the column "% $MnO_2$ present."

<div align="center">TABLE II.</div>
<div align="center">Analysis of Precipitated Manganese Dioxide Products.</div>

| Character of sample. | | % $MnO_2$. | |
|---|---|---|---|
| | | Found. | Present. |
| (1) Weldon mud........................................ | (a) | 50.40 | 50.40 |
| | (b) | 50.42 | ... |
| (2) Precipitated by reducing potassium permanganate........ | (a) | 80.90 | 80.86 |
| | (b) | 80.88 | ... |
| (3) Precipitated from sulfate solution by hydrogen peroxide... | (a) | 74.72 | 74.80 |
| | (b) | 74.76 | ... |
| (4) Precipitated by chlorate from nitrate solution............ | (a) | 98.10 | 98.00 |
| | (b) | 98.10 | ... |
| (5) Precipitated by hypochlorite from sulfate solution........ | (a) | 98.42 | 98.44 |
| | (b) | 98.58 | ... |

The results of Table II show the method to give accurate results for precipitated manganese dioxide.

A preliminary study was made to determine the most desirable concentration of iodide and phosphoric acid to be used for the decomposition of the natural oxides. 10 cc. of $N$ iodide and 10 cc. of 2 $N$ phosphoric acid were found to be a good proportion.

Many natural manganese ores react with difficulty with iodide in acid solution, while with the precipitated forms of manganese dioxide the reaction goes to completion almost immediately. 0.1 to 0.2 g. samples of pyrolusite in an Erlenmeyer flask covered with a watch glass were treated with 10 cc. of $N$ iodide and 10 cc. of 2 $N$ phosphoric acid, and were then diluted to 100 cc. and allowed to react for ten minutes. The iodine was then titrated with standard thiosulfate. When the titration was completed it was observed that the reaction had not gone to completion, because of the coarseness of the samples. Thereafter to overcome this difficulty, all ore samples were ground to pass through a 200-mesh silk sieve, thus increasing the surface exposure of the sample. When the iodine had been titrated the residue was examined carefully for undecomposed ore. If any such remained the precipitate was allowed to settle, and after the solution had been carefully decanted, the residue was washed once by decantation, and again treated with phosphoric acid and iodide, and titrated. In most cases the amount of 0.1 $N$ thiosulfate required for the

[1] *Ann.*, **86**, 283 (1853).

second treatment with acid and iodide was small in amount, seldom being more than 0.2 cc. However, some pyrolusite samples, especially those containing considerable iron oxide, were found to be attacked with difficulty by this process. Such samples cannot be analyzed successfully by this method. Hence, if the character of the ore is unknown a qualitative test should be first made to ascertain if the method will give a satisfactory reaction with the ore. Some typical analyses are given in Table III.

TABLE III.

Analysis of Pyrolusite.

| Sample No. | % available oxygen. | |
| --- | --- | --- |
| | Found. | Present. |
| 1........................................ | 14.91 | 14.89 |
| 2........................................ | 13.28 | 13.32 |
| 3........................................ | 10.22 | 10.26 |
| 4........................................ | 2.10 | 2.06 |
| 5........................................ | 12.81 | 12.90 |
| 6........................................ | 15.43 | 15.50 |

Number 1 of Table III was a sample of "wad" and it reacted almost immediately. The other five samples were samples of pyrolusite and required about fifteen minutes for decomposition. A second treatment with acid and iodide was required for Samples 3, 5 and 6. A blank on the reagents required only 0.02 cc. of thiosulfate after standing fifteen minutes. The percentages of "Available Oxygen—Present" were obtained by the distillation method of Bunsen.

All attempts to adapt this method to the determination of manganese have been unsuccessful because of the fact that either manganese could not be precipitated as pure manganese dioxide or the excess of oxidizing agent could not be successfully removed. However, the method gave the correct percentage of available oxygen contained in all such products analyzed. With hydrogen peroxide the precipitation of the manganese could be made complete, but the resulting product was low in available oxygen. This shows that hydrogen peroxide has a reducing effect upon the manganese dioxide or prevents the formation of pure manganese dioxide initially. Friedheim and Brühl[1] have also called attention to this effect.

With hypochlorite and hypobromite the principal difficulty encountered was in removing the excess of oxidizing agent. Boiling or filtering required too long periods of time. Phenol removed the chlorine but caused the appearance of a colored solution which obscured the end point. When a product was obtained free from chlorine or bromine it also contained too little available oxygen. Chlorate, persulfate and bromate were also found unsatisfactory.

From this work one can conclude that such oxidized manganese products

[1] Z. Anal. Chem., 38, 681 (1899).

as are decomposed by the phosphoric acid and potassium iodide reaction can be analyzed with rapidity and the results are accurate. Manganates, permanganates and precipitated oxides fall into this class. The method finds application also to the more easily decomposed pyrolusite ores. With some pyrolusite samples, especially those containing a large amount of iron oxide, considerable care must be taken to insure a complete reaction. For such samples the method is not recommended.

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## TITRATION OF MAGNESIUM.

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*This paper deals with the titration of magnesium as applied to water analysis.* Two methods are available, one consisting in the precipitation of magnesium as magnesium-ammonium phosphate and titration with $0.10 N$ HCl after filtration; the other in the precipitation as magnesium-ammonium arsenate and titration of the iodine liberated after treating with acid and KI.

Stolba[1] suggested that magnesium be determined by titrating the precipitate of magnesium-ammonium phosphate with HCl, using methyl orange as indicator, assuming that one mol of $MgNH_4PO_4$ requires 2 mols of acid. Mead[2] speaks of the accuracy of the method, but points out that nothing is gained by using it owing to the tediousness of washing with alcohol. Cohen,[3] however, besides mentioning the difficulty of washing, also reports that it is impossible to obtain concordant results.

After working on this method for some time, we overcame the difficulty of washing the precipitate by filtering with aid of suction, using a "Black Ribbon" filter with a protected cone. Concordant results, however, were not always obtained when the precipitate produced by the usual procedure was titrated, *i. e.*, when the precipitation was made directly in the solution from which the calcium had been removed. Since extreme care was taken to remove all the free ammonia, we concluded that the errors came from impurities in the precipitate. The success of the method depends entirely upon the complete precipitation of the magnesium as pure $MgNH_4PO_4$. The conditions for such a precipitation have been pointed out by Gooch and Austin,[4] and by Neubauer.[5] These are, that the solution be neutral and as free as possible from ammonium salts, and that the

[1] *Chem. Centr.*, 1866, 728.
[2] THIS JOURNAL, 21, 746 (1899).
[3] *Ibid.*, 29, 1464 (1907).
[4] *Am. J. Sci.*, [4] 7, 187 (1899).
[5] *Z. angew. Chem.*, 9, 839 (1896).