ANALYSIS OF MANGANESE AND MANGANESE DIOXIDE

PART 3. IMPROVEMENTS IN THE ANALYTICAL METHOD OF MnO_2

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Introduction

In the chemical analysis of available oxygen of manganese dioxide, a powdered sample is heated with an acid solution of reducing agent such as arsenite, oxalate, HCl or ferrous sulfate.[1] Though the time required for the complete dissolution varies depending on the particle size and kind of the sample, generally it takes one hour to 3 hours.[2] In H_2O_2 method,[3] MnO_2 can be dissolved rapidly without heating, but the method is not applicable for all the samples since impurities in MnO_2 decompose H_2O_2 in H_2SO_4. Recently the author[4] found that magnetic stirring hastens the dissolution rate of MnO_2 by an acid ferrous sulfate solution even at room temperature. Table 1 shows the comparision of the dissolution time required in both methods, the current boiling method and the magnetic strring method, with various samples. It is clear that the magnetic stirring method takes only 1/3 to 1/9 time of the boiling method in spite of non-heating. In the dissolution of MnO_2 by acid $FeSO_4$ solution at room temperature, CO_2 atmosphere is not necessary, while it is necessary in case of the boiling method.

In order to find the most accurate and fairly rapid method for the MnO_2 analysis, a method,[5] in which available oxygen and total manganese can be determined in one sample, is examined using the $FeSO_4$ method with magnetic stirring for available oxygen and a potentiometric titration[6] for the total manganese determination. It was found that if the neutralization in the procedure is carried out with special care, very accurate results should be obtained and that the method could be applied satisfactorily to manganese dioxide containing much chloride

TABLE 1. Comparison of the Dissolution Time in which 200 mg of Each MnO_2 was Placed into a 125 ml Elrenmyer Flask Containing 25 ml of 0.5 M $FeSO_4$ in 3.6 N H_2SO_4

Sample	Time required for a complete dissolution	
	Boiling (min.)	Magnetic stirring (min.)
No. 1 Electrolytic MnO_2	18	2
No. 2 Natural ore	24	6
No. 3 Natural pyrolusite	30	10
No. 4 Standard Sample 25 *b*	32	4
No. 5 Pure β-MnO_2 from $Mn(NO_3)_2$	35	8

In the one method it was boiled gently and in the other it was stirred by magnetic stirring at room temperature (25° C). Sample No. 1, 2, 3 were ground to pass through 100 mesh sieve.

ion (for example, a cathode mixture of Leclanché type dry cell), if mercuric sulfate is used as a masking agent of the chloride ion.

Neutralization methods

In the combined procedure for determination of available oxygen and total manganese in one sample, which will be described in the following section, after the determination of available oxygen, the solution containing manganese (II) ion, ferric ion and much sulfuric acid must be neutralized to adjust the pH to 6 to 7, which is the optimum condition for the potentiometric titration of manganese (II) ion.[6] This neutralization process was examined as follows: A 250 ml beaker was set on a magnetic stirring equipment, into which a ferric sulfate solution, a manganese (II) sulfate solution, sodium pyrophosphate, water and KOH (pellets) were added in the order shown in Table 2 in each experiment, then the final solution was titrated with 0.1000 N $KMnO_4$ standard solution potentiometrically by using Pt electrode as the indicator electrode. The abrupt potential change of the Pt electrode occurred from 0.4 to 0.5 volt vs. saturated calomel electrode.

From the results of Exp. 1, 2 and 3, it seems that a small portion of manganese (II) ion is oxidized to manganese (III) ion during the neutralization if a large amount of ferric ion is present in the solution. Exp. 4 shows no air oxidation of Mn^{II} to Mn^{III} by exposing the solution to air under stirring. Exp. 5, in which the acid was neutralized only by the pyrophosphate, shows correct results. Exp. 7 in which a large portion of the acid was neutralized in a small volume, also shows correct results. This may mean that dissolved oxygen oxidize Mn^{II} to Mn^{III} during the neutralization only when a local pH raise is extreme. Exp. 8 shows no influence of Hg^{++} ior in this potentiometric titration. From these results, two methods are recommended for the neutralization; 1) to neutralize with pyrophosphate only, 2) neutralize about half of the acid by KOH in a small volume of the solution, then dilute to 200 ml and complete the neutralization by using $Na_4P_2O_7 \cdot 10H_2O$.

TABLE 2. Neutralization Method

Addition order		Consumed 0.1 N $KMnO_4$ (ml)	Deviation** (ml)
Exp. 1	1 25 ml of 0.25 M $Fe_2(SO_4)_3$ in 3.6 N H_2SO_4 2 10 ml of 0.16 M $MnSO_4$ 3 27 g of $Na_4P_2O_7 \cdot 10H_2O$ 4 H_2O to make 200 ml soln. 5* 15 pellets of KOH to adjust pH to 6	19.90 19.88	−0.17 −0.19
Exp. 2	The same condition as Exp. 1 Except slow magnetic stirring During the addition of KOH	19.80 19.75	−0.27 −0.35
Exp. 3	1 25 ml of the $Fe_2(SO_4)_3$ soln. 2 27 g of $Na_4P_2O_7 \cdot 10H_2O$ 3 H_2O to make 200 ml soln. 4 15 pellets of KOH 5 10 ml of 0.16 M $MnSO_4$ (after disappearing yellow color of $Fe(OH)_3$)	20.09 20.10	+0.02 +0.03

TABLE 2. (*Continued*)

	Addition order	Consumed 0.1 N $KMnO_4$ (ml)	Deviation** (ml)
Exp. 4	The same condition as Exp. 3 Except that after addition of $MnSO_4$ the solution was left under stirring for 2 hours, then it was titrated	20.07 20.10	+0.00 +0.03
Exp. 5	1 25 ml of the $Fe_2(SO_4)_3$ soln. 2 10 ml of 0.16 M $MnSO_4$ 3 H_2O to make 200 ml soln. 4 $Na_4P_2O_7 \cdot 10\,H_2O$ until pH6 is obtained, of which about 35 g was necessary	20.07 20.08	+0.00 +0.01
Exp. 6	1 25 ml of the $Fe_2(SO_4)_3$ soln. 2 10 ml of the $MnSO_4$ soln. 3 H_2O to make 200 ml soln. 4 15 pellets of KOH 5 27 g of $Na_4P_2O_7 \cdot 10\,H_2O$ (to bring pH to about 6)	20.05 20.02 19.98	−0.02 −0.05 −0.09
Exp. 7	1 25 ml of the $Fe_2(SO_4)_3$ soln. 2 10 ml of the $MnSO_4$ soln. 3 15 pellets of KOH 4 H_2O to make 200 ml soln. 5 27 g of $Na_4P_2O_7 \cdot 10\,H_2O$	20.08 20.09	+0.01 +0.02
Exp. 8	1 25 ml of the $Fe_2(SO_4)_3$ soln. 2 10 ml of the $MnSO_4$ soln. 3 1 g of $HgSO_4$ 4 H_2O to make 200 ml soln. 5 40 g of $Na_4P_2O_7$ to bring pH to 6	20.05 20.06	−0.02 −0.01

* Temporary precipitation of $Fe(OH)_3$ appears due to the local raise of pH.

** Deviation from 20.07 which was obtained by separate two titrations of the $Fe_2(SO_4)_3$ solution and the $MnSO_4$ solution.

The recommended procedure for MnO_2 analysis

A weighed sample (about 200 mg) is transferred into a 125 ml Erlenmeyer flask. 25 ml of 0.25 M $FeSO_4$ in 3.6 N H_2SO_4 is added to it, then the mixture is stirred by a magnetic stirrer at room temperature until complete dissolution (usually several minutes). Then the stirring bar is taken out of the solution by applying a big magnet from outside, and washed with water. Titrate the solution with 0.1 N $KMnO_4$ standard solution (a ml). The solution after titration is transferred into a 250 ml beaker and neutralized to pH 6–7 as described above by using $Na_4P_2O_7 \cdot 10\,H_2O$. Titrate the solution potentiometrically with the same 0.1 N $KMnO_4$ as that used for the available oxygen determination (the potential change at the end point takes place from about 0.4 volt to 0.5 volt vs. saturated calomel electrode). Calculate the available oxygen content and total manganese content from the following equations:

$$\mathrm{O}\% = \frac{8 \times \mathrm{N}(b-a) \times 100}{(\text{Sample, mg})\left(1 - \frac{\mathrm{M}}{100}\right)}\ \%$$

where N : Normality of $KMnO_4$
M : moisture content (%)
b : ml of $KMnO_4$ consumed when 25 ml of the $FeSO_4$ soln. is titrated.
a : ml of $KMnO_4$ consumed in the available oxygen titration.

$$\text{Mn}\ \% = \frac{54.94\left(a' - \frac{a}{4}\right) \times \frac{\text{N}}{5} \times 4 \times 100}{(\text{Sample, mg})\left(1 - \frac{\text{M}}{100}\right)}\ \%$$

where a' : ml of $KMnO_4$ consumed in the potentiometric titration.

The results for the standard sample 25 *b* from the National Bureau of Standards (USA) are shown in Table 3. The results agree with the standard values within one part per 1,000. The whole process takes only 15 to 18 minutes.

TABLE 3. Analyzes of Standard sample 25 *b*

No.	Sample taken (mg)	$KMnO_4$ (a) (ml)	($b-a$)	O (%)	Deviation* (%)
1	199.5	25.52	41.26	16.68	+0.01
2	199.7	25.49	41.29	16.67	0.0
3	200.3	25.38	41.40	16.66	−0.01
4	200.6	25.32	41.46	16.66	−0.01
5	200.7	25.25	41.53	16.68	+0.01

b=66.78. * Deviation from 16.67, the standard value.

No.	$KMnO_4$ (a') (ml)	$\left(a' - \frac{a}{4}\right)$	Mn (%)	Deviation** (%)
1	32.68	26.30	58.38	+0.03
2	32.72	26.35	58.26	−0 09
3	32.70	26.40	58.40	+0.02
4	32.73	26.40	58.30	−0.05
5	32.80	26.49	58.47	+0.12

** Deviation from 58.35, the standard value.

Analysis of MnO_2 in the presence of NH_4Cl

In the study of MnO_2 for Leclanché dry cell, it occurs frequently to analyze manganese dioxide containing chloride. Each 200 mg of the standard sample was mixed with 2 ml of NH_4Cl solution in various concentration in an Erlenmyer flask

TABLE 4. Analyses of Manganese Dioxide in the Presence of NH_4Cl

No.	Digesting solution	O (%)	Deviation* parts per 1,000	Mn (%)	Deviation** parts per 1,000
1	2 ml of H_2O	16.63	−2.4	58.49	+2.3
2	2 ml 4 M NH_4Cl	16.64	−1.7	58.51	+2.7
3	2 ml of 2 M NH_4Cl	16.64	−1.7	58.53	+3.0
4	2 ml of 1 M NH_4Cl	16.63	−2.4	58.34	−0.2
5	None	16.64	−1.7	58.45	+1.7

* Standard value=16.67. ** Standard value=58.35.

and kept in it overnight. Then the mixture was analyzed in the procedure recommended above. Before the titration for the available oxygen, 1 g of $HgSO_4$ was added. The results are shown in Table 4, in which the data agrees with the standard values within 3 parts per 1,000.

References

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