

ANALYSIS OF MANGANESE AND MANGANESE DIOXIDE

PART 2. A SIMPLE AND RAPID VOLUMETRIC METHOD FOR DETERMINATION OF MANGANESE AND ITS APPLICATION TO IRON AND STEEL ANALYSIS AND MANGANESE ANALYSIS IN MnO_2

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I. Introduction

Many methods have been proposed for volumetric determination of manganese, *e.g.* the sodium bismuthate method, the persulfate method, the Volhard method, the silver peroxide method and others, among which it is thought that the bismuthate method is the most accurate. It has been adopted as the standard method for determination of manganese in iron and steel though the method contains a time-consuming filtration process.

Recently H. Kiyota and T. Yamamoto¹⁾ reported that sodium bismuthate decomposes easily with liberation of oxygen gas in sulfuric acid in the presence of silver ion. Therefore, the reagent is applicable to the colorimetry of manganese as a convenient oxidizing reagent.

The writers traced it again using a sodium bismuthate powder bought as analytical reagent for manganese, to confirm whether the decomposition of sodium bismuthate in the presence of silver ion is perfect or not. It was made clear that addition of a small amount of silver ion accelerates the decomposition very much, but it was not complete in a short time even at higher temperatures (50° – 70°C). However, in this case the solution becomes clear within 10 to 30 minutes, owing to rapid sedimentation of the coarse bismuthate particles and the rapid decomposition of small particles suspended.

In the present study, the writers devised a simple method for manganese determination, basing on the above facts. Manganous ion is oxidized to permanganate ion by sodium bismuthate, then silver ion is added which acts as catalizer to decompose the excess reagent. The solution is diluted to a known volume and is allowed to stand; then a portion of the supernatant solution is taken out and titrated with standard permanganate solution after adding ferrous sulfate solution.

This method is very simple without any heating and filtration and is particularly effective to treat a large number of samples.

II. Sedimentation and Decomposition of Sodium Bismuthate

In the proposed method, it is necessary that the excess sodium bismuthate in the solution should be decomposed and precipitated as quickly as possible. In order to investigate the dependence of the velocity on the silver ion concentration,

sulfuric acid concentration and the temperature, the following experiments were carried out.

(1) *The amount of silver ion added*

50 ml of 6 N H_2SO_4 , 0 to 5 ml of Ag_2SO_4 saturated solution (c.a. 0.047 N) and about 40 ml of water were taken into a 100 ml. volumetric flask together. 500 ± 5 mg of NaBiO_3 powder was added there, then the flask was filled up with water to the mark. After overturning it five times, it was allowed to stand at room temperature which is not far from 15°C . 30 and 50 minutes later, 25 ml portions were pipetted and titrated with KMnO_4 standard solution (0.05 N) after addition of 10 ml of ferrous sulfate solution. Table 1 shows the results.

TABLE 1. Influence of the Amount of Silver Ion Added

Ag ₂ SO ₄ added (ml)	KMnO ₄ consumed (ml)	
	After 30 min.	After 50 min.
0.0	21.95	22.27
0.5	22.20	22.65
1.0	22.40	22.64
2.0	22.64	22.63
3.0	22.63	22.63
5.0	22.65	22.65

Blank=22.65 (this was measured after filtering the above supernatant solution passed through G4-glass filter.)

In the absence of any silver ion, the supernatant solution shows a considerable oxidizing power owing to the residual bismuthate even after 50 minutes. While in the presence of more than 2 ml of silver sulfate solution, 30 minutes later there was not any significant differences from the blank. This means that silver ion decomposes catalytically the suspended bismuthate.

(2) *The sulfuric acid concentration*

In the procedure described above, the influence of the acidity was examined with constant silver sulfate (2 ml). Table 2, showing the results, indicates that the higher the acidity is, the larger is the decomposition velocity.

TABLE 2. Influence of the Acidity

Acidity in H ₂ SO ₄ (N)	KMnO ₄ consumed (ml)	
	After 20 min.	After 40 min.
1	22.05	22.61
2	22.05	22.63
3	22.30	22.60
4	22.62	22.61
5	22.61	22.60

The oxidation of manganous ion to permanganate ion by NaBiO_3 is suitable at the acidity of 2 to 4 N, therefore 4 N in acidity seems to be preferable in this procedure.

(3) *Influence of the temperature on the decomposition rate*

The same procedure as described in (1) was used.

In this experiment, 2 ml of the silver sulfate solution and a constant acidity (4 N) were always adopted. The lower part of the volumetric flask was dipped into the water kept at a constant temperature for an hour before addition of NaBiO_3 and silver ion. From Table 3 showing the results, the decomposition velocity of the NaBiO_3 suspension is found to increase with the increased temperature. At 33°C only 10 minutes is sufficient to have a constant value. Even in winter season, if we use conc. H_2SO_4 in order to adjust the acidity, it will be very easy to raise the temperature to 30°C or higher and to keep it for ten minutes.

TABLE 3. Influence of the Temperature

Temperature (°C)	KMnO ₄ consumed (ml)		
	After 10 min.	After 30 min.	After 50 min.
33	22.65	22.63	22.65
22	22.32	22.58	22.60
14	21.40	22.40	22.60
4	19.60	21.80	22.48

(4) *On the blank*

There is small difference between the blank value which is measured by the procedure recommended below without sample, and the amount of KMnO_4 consumed by a direct titration of 10 ml of ferrous sulfate solution, as shown in Table 4. The results show that the blank value depends largely on the amount of sodium bismuthate used and not on the standing time (15-50 min.) and the temperature (32°-42°C). The supernatant solution is a little turbid after 20 minutes' standing and it becomes completely clear after 50 minutes. However, the two blanks are almost equal.

TABLE 4. The Blank Values Under Various Conditions

Temp. (°C)	Added in 100 ml	NaBiO ₃	0.1 N FeSO ₄ added (ml)	KMnO ₄ consumed (ml) standing time (min.)				
				10	15	20	25	50
30	10 ml of conc. H_2SO_4	0.5	10	19.09	—	19.11	—	19.10
30	10 ml of conc. H_2SO_4	1.0	10	18.70	—	18.90	—	18.90
40	20 ml of mixed acid*	0.5	10	—	19.12	—	19.12	—
40	20 ml of mixed acid*	1.0	10	—	19.00	—	19.00	—
15	None	0	10	19.40	—	—	—	—

* Used later for dissolving one g of iron and steel.

It is desirable to prepare or to select a good sodium bismuthate that has no blank. At any rate, it is now necessary to try a blank run using a definite amount of sodium bismuthate under the same condition as the actual analysis.

III. Recommended Procedure

Take a suitable amount of sample solution (Mn: 3 to 20 mg), some water and

sulfuric acid into a 100 ml-volumetric flask together, so that the content should have about 90 ml in volume and is about 4 N in acidity. It is desirable to bring the temperature of the solution to 30° to 40° C by a suitable concentration of sulfuric acid (6-36 N). If necessary, dip the flask in the water kept at the desired temperature. Then add 0.5 ± 0.05 g of NaBiO_3 and shake vigorously for 4 to 5 seconds. 30 to 60 seconds later, add 2 ml of the saturated solution of Ag_2SO_4 (0.047 N) to the mixture and fill up with water to the mark. Then overturn it with the stopper five times, take off the stopper and allow it to stand for 10 to 30 minutes. Remove slowly a 50 ml portion of the supernatant with pipette to a beaker and add a known amount of ferrous sulfate solution. Titrate the excess ferrous ion with KMnO_4 standard solution (0.05 N). If the amount of KMnO_4 consumed in a ml and the blank, treated as above without the sample, b ml., the manganese in the sample can be calculated as follows:

$$\text{Mn mg} = 54.93 \times \left(\frac{(b-a) \times N}{5 \times 1,000} \right) \times \left(\frac{100}{50} \right) \times 1,000 = 21.97(b-a)N$$

N: Normality of KMnO_4 .

Table 5 shows the results of determined manganese in manganese sulfate solution by the above procedure with varying standing time after addition of silver ion. Most of these results agree with the standard value by the current bismuthate method within the error of one per cent. And even after six hours' standing, the value was almost constant. It seems to be preferable to allow the solution to stand more than 20 minutes when one gram of sodium bismuthate is used or the temperature is lower than 30° C.

TABLE 5. Determination of Manganese in Manganese Sulfate (at 32° C)

Mn taken* (mg)	Mn found (mg) standing time				
	10 min.	20 min.	50 min.	2 hr.	6 hr.
7.36	7.28	7.28	7.32	—	—
14.73	14.74	14.65	14.71	14.70	14.65
29.46**	29.81	29.43	29.37	—	—

* This manganese sulfate solution was standardized by the current bismuthate method.

** 1.0 g of NaBiO_3 , was used.

IV. Application of the Present Method to Analysis for Iron and Steel

Determination of manganese in iron and steel was carried out by the following procedure.

A 1.00 g sample is transferred to a 100 ml Erlenmyer flask and dissolved in 20 ml of a mixed acid (1,000 ml of 18 N- H_2SO_4 + 120 ml of conc. HNO_3) and 20 ml of water by heating, and the solution is boiled for about one minute. Then the solution is transferred to a 100 ml volumetric flask and some water is added to bring the volume of the solution to about 90 ml. and the flask is placed in water at a known temperature (30, 42 and 49° C). The remaining procedure is the same

as in the preceding section. The results are shown in Table 6. Of course the blank must be carried out.

TABLE 6. Determination of Manganese in Iron and Steel

Standard Sample	Temp. (°C)	Standard value (mg)	Mn found (mg)			
			10 min.	15 min.	25 min.	35 min.
Carbon steel I	30	7.17	7.19	7.06	7.12	7.04
	42		7.12	7.14	7.08	7.11
	49		6.79	6.55	6.22	6.00
Carbon steel II	20	4.12			4.14	
	20				4.18	
Cast iron	20	7.74			7.64	
	20				7.66	

The results obtained at 30° and 42° C are good, though they are a little low owing to the rusting of carbon steel I. But at 49° C the manganese value decreases with time, this shows the decomposition of permanganate ion. Therefore, the oxidation of manganese and the standing must be at 20° to 40° C. In the case of cast iron that contains 4.08% of carbon, the carbon is usually filtered off before the oxidation process. But in the present method, this filtration is dispensable.

This method is not a very accurate one but very simple and the whole analysis takes only 18 minutes. Particularly when many samples are analyzed this method may be very effective.

V. Application to MnO₂ analysis

Solutions, reagents and apparatus:

- 1) 0.5 N FeSO₄ in 3.6 N H₂SO₄
- 2) 0.1 N KMnO₄
- 3) 6 N H₂SO₄
- 4) Ag₂SO₄ saturate solution
- 5) Sodium bismuthate
- 6) 100 ml volumetric flask, 100 ml Erlenmeyer flask.

Procedure for available oxygen:

Take 200±0.3 mg of a sample in 50 ml Erlenmyer flask and add 20 ml of 0.5 N FeSO₄ solution and an iron piece covered by teflon resin. Then stir it magnetically. After complete dissolution, transfer the solution into 100 ml volmetric flask and fill with water to the mark. Take out a 50 ml portion of the solution and titrate with 0.1 N KMnO₄ solution (A ml). MnO₂ content can be calculated by the following equation:

$$\text{MnO}_2 \text{ mg} = \left(\frac{\text{MnO}_2}{2} \right) \times 2(B - A)_N = 43.465 \times 2(B - A)_N$$

N: Normality of KMnO₄

B: ml of KMnO₄ consumed by 10 ml of the 0.5 N FeSO₄.

TABLE 7. Results for Available Oxygen (Standard Sample No. 25 b from National Bureau of Standards)

Condition of dissolution total vol. (ml)	Time required for dissolution	MnO ₂ content		
		Found (mg)	(%) ⁺	Standard value (%)
1. No stirring 20	18 hrs.	181.3	91.37	90.59
2. No stirring 20	18	180.0	90.73	
3. No stirring 20	18	180.3	90.87	
4. Magnetic st. 20	7 min.	179.8	90.62	
5. Magnetic st. 40*	7	180.0	90.72	
6. Magnetic st. 90*	7	180.0	90.72	
7. Magnetic st. 90**	10	180.4	90.92	

* After addition of 20 ml of FeSO₄, 3.6 N H₂SO₄ was added to make the volume.

** After addition of 20 ml of FeSO₄, 70 ml of water was added. Therefore, the solution is 0.1 N in ferrous ion and 0.8 N in hydrogen ion.

+ These values were calculated by taking the moisture content of the sample into consideration, that is, the moisture content was 0.8% when measured as the direction, for 1 hour at 120° C.

Procedure for total manganese:

Transfer a 20 ml portion of the above solution, of which 50 ml remains, into another 100 ml volumetric flask and add 60 ml of 6 N H₂SO₄ and 10 ml of water and then add 1.0±0.05 g of sodium bismuthate powder to the solution. Shake 5 to 10 second, then add 2 ml of silver sulfate solution and fill the volumetric flask with water to the mark and mix the contents well. After standing still for 15 to 20 minutes (the temperature of the solution is preferable to be kept at 30 to 40° C, because at lower temperatures it takes much more time), a 50 ml portion of the supernatant solution is taken out and 5 ml of 0.5 N FeSO₄ solution is added and the excess ferrous ion is titrated with 0.1 N KMnO₄ (A ml). Manganese in the original sample can be calculated as follows:

$$\text{Mn mg} = \frac{\text{Mn}}{5} \times (B - A) \times 2 \times 5 \text{ N} = 10.986(B - A) \times 10 \text{ N}$$

N: Normality of KMnO₄

B: Blank value after all the above procedure only with 4 ml of 0.5 N FeSO₄ solution. This is because sometimes FeSO₄ reagent contains manganese as impurity and also sodium bismuthate brings small amount of blank.

TABLE 8. Results of Total Manganese

0.1 N KMnO ₄ consumed (ml)	Found (mg)	Mn content (%)*	Standard value (%)
1. 14.98	115.5	58.21	58.35
2. 14.96	115.7	58.31	
3. 14.97	115.6	58.26	
4. 15.00	115.3	58.11	
5. 15.00	115.3	58.11	
6. 14.97	115.6	58.26	

B=25.49 ml, 0.5 N FeSO₄ 5 ml ⇒ 25.60 ml of 0.1 N KMnO₄

* These values were calculated by considering moisture content.

The results of both available oxygen and total manganese show a good agreement with the standard values. The use of magnetic stirring in the dissolution process is very effective irrespective of concentration of ferrous ion as well as hydrogen ion, and it enables the process to get a rapid determination without any heating. This will be described in part 3 of this paper in details.

Reference

- 1) H. Kiyota and T. Yamamoto: J. Chem. Soc. Japan, pure Chem. sect. **76**, 1179 (1955).