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Determination of Manganese in Iron, Steel and Ferromanganese. II

Determination of Manganese in Ferromanganese*

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Synopsis

The suitable concentration of acids and other conditions in ferrous-permanganate method after oxidation with persulfate for the determination of manganese in ferromanganese were studied and the following results were obtaind. (1) On the relation between the amount of manganese and the requisite amount of phosphoric acid, using about 2 g of ammonium persulfate in total volume of 200 ml, the amount of phosphoric acid added must be increased with the increase of manganese content. But the amount of phosphoric acid necessary was smaller, when the total volume is made to 400 ml and 4 g of ammonium persulfate are used. (2) On the concentration of the acid, using 4 g of ammonium persulfate in total volume of 400 ml, 4~28 mg of manganese was determined in the concentration range of 1.4~2.6 N H_2SO_4 or 0.6~1.0 N mixed acid of H_2SO_4 and HNO_3 (3 : 1). (3) Boiling the solution for 1~5 minutes gave quantitative results while a somewhat lower values were obtained when boiled more than 6 minutes. (4) From the above results, the suitable analytical procedures for the determination of manganese in ferromanganese were established and the analysis of several actual samples were carried out and good results were obtained.

I. Introduction

For the determination of manganese in ferromanganese, the sodium bismuthate and the Volhard's methods have been used but the procedures of the former method is rather tedious and requires a long time, moreover, sodium bismuthate being rather expensive, and the latter method is not accurate. The present writers, continuing the experiments reported in the previous paper(1), examined the various conditions of the method that have been carried out in this laboratory, the oxidation with ammonium persulfate and reduction with the excess of ferrous sulfate and then back titration with potassium permanganate. As the results, necessary conditions for the determination of manganese in ferromanganese were clarified and the details are described herein. The procedures of the present method were much more simple and the accuracy was better than the sodium bismuthate method.

II. Fundamental experiments

1. Reagents

(a) Standard manganese solution: Manganese sulfate solution (Mn 1.056mg/ml) was used. Content of manganese was determined by the sodium bismuthate method.

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* The 781st report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Japan Institute of Metals, 17-4 (1953), 194.

(1) H. Gotô and S. Watanabe, Sci. Rep. RITU, A 6 (1954), 1.

(b) 0.1N ferrous ammonium sulfate solution: It was prepared from ferrous ammonium sulfate crystals and the normality was determined by titration with standard 0.1 N potassium permanganate solution.

(c) Standard 0.1 N potassium permanganate solution : It was prepared by the usual method from potassium permanganate crystals and standardized with sodium oxalate.

2. Experimental procedures

Various amounts (4~28 mg of Mn) of standard manganese solution was added to sulfuric acid solution or a mixture of sulfuric and nitric acids. To such a solution, 5 ml of 2 per cent silver nitrate solution and various amounts (approx. 1~16ml) of phosphoric acid were added, the whole volume was brought to about 200 or 400 ml with the addition of water, and the solution was boiled after the addition of 2 or 4 g of ammonium persulfate to oxidize manganese. After decomposing the excess of the persulfate, the mixture was cooled, excess of 0.1 N ferrous ammonium sulfate was added, and the solution was back titrated with 0.1 N potassium permanganate solution to determine the amount of manganese. When a sample of ferromanganese is analyzed by the foregoing procedures, the iron content in the final solution is around 0.025 g so that when a large amount of manganese was present, no addition of iron was made.

3. Amount of manganese and phosphoric acid

(a) With a small amount of manganese: In order to examine the requisite amount of phosphoric acid for iron and steel samples containing a small amount of manganese, metallic iron (Fe 1 g) was added to the sulfuric, nitric or sulfuric plus nitric (3 : 1) acid solutions of the most moderate concentration and was dissolved (the acid required to dissolve iron is added separately). 10 ml of the standard manganese solution (11.19 mg Mn), sufficient quantity of water, 5 ml of 2 per cent silver nitrate solution, 2 g of ammonium persulfate and various amounts of phosphoric acid (sp. gr. 1.7) were added to the solution and the whole volume of the solution was brought to about 200 ml. This solution was heated to oxidize manganese, boiled for about 2 minutes after large bubbles began to rise, and the mixture was cooled. Manganese was then determined by the method as in the foregoing experimental procedures and the results thereby obtained are shown in Fig. 1. As can be seen from this graph, good results are obtained by the addition of above 4 ml of phosphoric acid (sp. gr. 1.7) when 1 g of iron and about 10 mg of manganese are present, but the values tend to become lower when the amount of phosphoric acid is less than 3 ml.

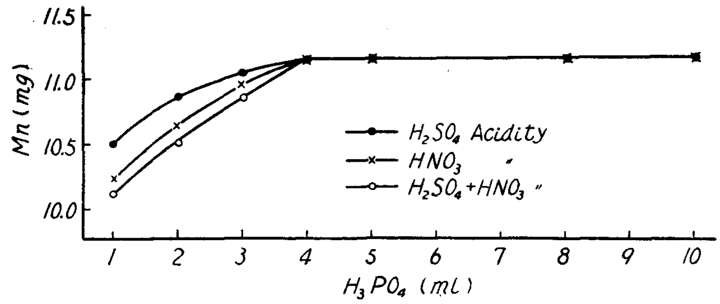

Fig. 1.

(b) With a large amount of manganese : According to the results obtained and described in the previous report, the concentration of sulfuric acid was maintained at the most moderate concentration (1.8 N). In this sulfuric acid solutions, experiments were carried out by the same procedure as above, adding various amounts of the standard manganese solution, sufficient quantity of water, 5 ml of 2 per cent silver nitrate solution, various amounts of phosphoric acid and 2 or 4 g of ammonium persulfate for 100 ml total volume. The results, as shown in Fig. 2, showed that at around 8 mg of manganese, 1 ml of phosphoric acid is sufficient but with the increased content of manganese, larger amount of phosphoric acid is required. In the case of 4 g of ammonium persulfate and about 8 mg of manganese, 1 ml of phosphoric acid is sufficient, while even with about 26 mg of manganese, about 5 ml of phosphoric acid is enough to give a quantitative result. In the case of a mixed solution (3 : 1) of sulfuric and nitric acids, the most suitable concentration (1.08 N) determined in the previous experiments was employed. Namely to this acid mixture, various amounts of standard manganese solution was added and this was treated as in the case of sulfuric acid solution only to determine the requisite amount of phosphoric acid for the determination of manganese. As shown in Fig. 2, the results indicated that the amount of phosphoric acid required to give a sufficient quantitative results was smaller than that in sulfuric acid solution.

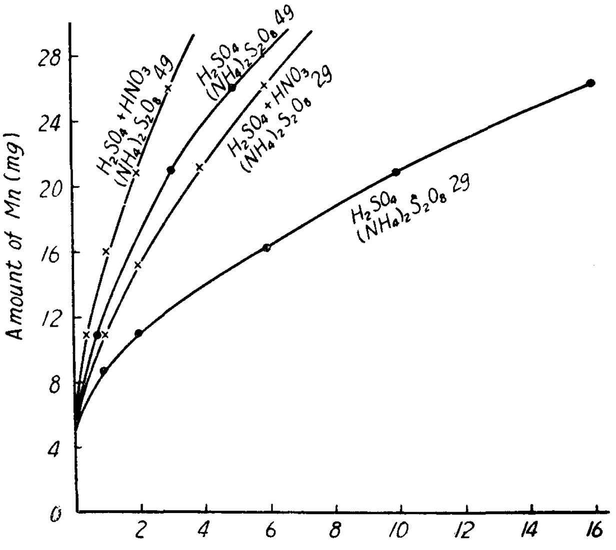

Fig. 2.

(c) With a total volume of 400 ml: Using various acid solutions, the total volume was brought to about 400 ml, 4 or 8 g of ammonium persulfate was added, and manganese was determined by the procedures as described above to obtain the requisite amount of phosphoric acid. The results are shown in Fig. 3, from which it is seen that about 7 ml of phosphoric acid is required with 26 mg of manganese and 4 g of ammonium persulfate in 1.80 N sulfuric acid solution, and about 4 ml of phosphoric acid is required with 8 g of ammonium persulfate. Using a mixture of sulfuric and nitric acids solution (1.08 N), 6 ml of phosphoric acid is sufficient with 4 g of ammonium persulfate and 26 mg of manganese, while it is required only 2 ml of phosphoric acid with 8 g of ammonium persulfate.

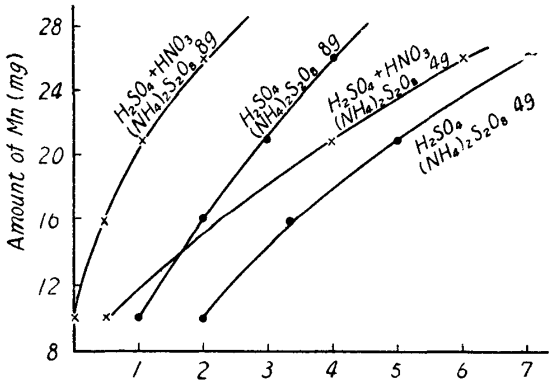

Fig. 3.

4. Concentration of the acid

(a) Sulfuric acid solution: Using 25 ml of the standard manganese solution (Mn 26.40 mg) it was performed the various concentrations of sulfuric acid solution with suitable quantities of water and sulfuric acid (12 N), then 5 ml of 2 per cent silver nitrate solution and 10 or 5 ml of phosphoric acid were added to it, and made up to about 400 ml of total volume. The experiments were then carried out with 4 or 8 g of ammonium persulfate to find out the range of sulfuric acidity in which manganese can be quantitatively determined. The results are shown in Table 1, from which it can be seen that the determination is possible in the range of 1.4～2.0N of sulfuric acid concentration when 4 g of ammonum persulfate is used and approximately 1.5～2.0 N when 8 g of ammonum persulfate is used.

Table 1. (Mn added : 26.40 mg)

Concentration of H_2SO_4 (N)	$(NH_4)_2S_2O_8$ 4 g		$(NH_4)_2S_2O_8$ 8 g	
	Mn obtained (mg)	Average (mg)	Mn obtained (mg)	Average (mg)
1.10	27.13 27.10 } 27.10 27.08	+0.70	28.42 28.38 } 28.35 28.26	+1.95
1.35	26.43 26.46 } 26.43 26.40	+0.03	27.14 27.10 } 27.13 27.16	+0.73
1.50	26.42 26.38 } 26.40 26.41	±0.00	26.40 26.45 } 26.42 26.42	+0.02
1.80	26.36 26.38 } 26.39 26.43	−0.01	26.44 26.40 } 26.42 26.42	+0.02
1.95	26.39 26.42 } 26.40 26.40	±0.00	26.42 26.46 } 26.44 26.44	+0.04
2.10	26.26 26.18 } 26.22 26.21	−0.18	26.22 26.20 } 26.23 26.28	−0.17
2.25	25.86 25.72 } 25.79 25.78	−0.68	25.72 25.64 } 25.69 25.70	−0.31

(b) Sulfuric and nitric acid (3 : 1) mixture: The same procedures as above were carried out with 25 ml of the standard manganese solution (Mn 26.40 mg) to find out the range of the acid concentration in which manganese can be quantitatively determined. The results are shown in Table 2 and it may be seen that the determination is quantitative in the range of 0.6～1.0 N of the mixed acid with 4 g, and 1.0～1.2 N of the acid with 8 g of ammonium persulfate.

The foregoing results indicate that the determinable range is more wider in sulfuric acid, so that 1.8 N of sulfuric acid solution, about 5 g of ammonium persulfate and 10 ml of phophoric acid were used for the subsequent experiments.

5. Boiling time

In accordance with the foregoing experimental results, the most suitable concentration of sulfuric acid (1.80N) was used with 25 ml of the standard manganese solution (26.40 mg Mn), 10 ml of phosphoric acid, 5 g of ammonium persulfate and 5 ml of 2 per cent silver nitrate solution, and the whole volume was brought to about 400 ml. This mixture was boiled for various lengths of time after large bubbles began to appear, then cooled rapidly, and manganese was determined by the usual experimental procedures. As can be seen from the results given in Table 3, the determination is quantitative up to approximately 5 minutes' boiling but the values become lower when boiled over 6 minutes.

Table 2. (Mn added : 26.40 mg)

Concentration of mixed acid (N)	$(NH_4)_2S_2O_8$ 4 g		$(NH_4)_2S_2O_8$ 8 g	
	Mn obtained (mg)	Average (mg)	Mn obtained (mg)	Average (mg)
0.52	27.26 27.30 } 27.26 27.23	+0.86	—	—
0.60	26.41 26.46 } 26.43 26.43	+0.03	—	—
0.81	26.42 26.45 } 26.42 26.40	+0.02	27.15 27.19 } 27.16 27.14	+0.76
0.90	26.43 26.44 } 26.43 26.43	+0.03	26.68 26.62 } 26.66 26.70	+0.26
0.98	26.41 26.43 } 26.42 26.40	+0.02	26.45 26.40 } 26.43 26.43	+0.03
1.10	26.38 26.43 } 26.41 26.42	+0.01	26.43 26.41 } 26.42 26.42	+0.02
1.18	25.87 25.93 } 25.89 25.88	−0.51	26.40 26.45 } 26.42 26.47	+0.02
1.30	24.64 24.68 } 24.68 24.72	−1.32	25.87 25.77 } 25.82 25.84	−0.58

Table 3. (Mn added : 26.40 mg)

Boiling time (min)	Mn obtained (mg)	Average (mg)
1	26.43 26.47 } 26.44 26.42	+0.04
2	26.45 26.42 } 26.42 26.40	+0.02
4	26.42 26.42 } 26.41 26.40	+0.01
5	26.40 26.41 } 26.39 26.38	−0.01
6	26.02 26.33 } 26.16 26.13	−0.24
7	25.90 25.98 } 25.91 25.86	−0.49

III. Determination of manganese in ferromanganese

Based on the foregoing experiments, following analytical procedures were devised.

1. Analytical procedures

In a 500 ml conical beaker, 0.25 g of the sample is weighed, about 30 ml of nitric acid (sp. gr. 1.4) is added and the mixture is heated to effect decomposition. Ten ml of sulfuric acid solution (1 : 1) is added, and the solution is evaporated until white fumes begin to generate, cooled, with water and warmed to dissolve the salts. After cooling, this solution is transferred to a measuring flask of 500 ml capacity, and diluted to the mark with water. To 50 ml of this solution, 40 ml of sulfuric acid solution (1 : 1), 5 ml of 2 per cent silver nitrate solution and 10 ml of phosphoric acid (sp. gr. 1.7) are added, and the whole volume is brought to about 400 ml. This mixture is boiled with about 5 g of ammonium persulfate until small bubbles change to large bubbles, then boiled further for 2 minutes until a large bubble comes up intermittently. After complete decomposition of ammonium persulfate by this boiling, the solution is cooled, about 10 ml of excess 0.1N ferrous ammonium sulfate solution is added, and the mixture is back titrated with 0.1N potassium permanganate solution. The quantity of manganese is calculated from the following equation:

$$\mathrm{Mn}(\%)=\frac{\{(0.1\mathrm{N\ FeSO_4(NH_4)_2SO_4ml}\times\mathrm{factor}-0.1\mathrm{N\ KMnO_4ml}\times\mathrm{factor})\}\times 10\times 0.1099}{0.25\ (\mathrm{g})}$$

2. Analytical results

Results obtained by the analysis of various samples by the above procedures are shown in Table 4.

Table 4.

Kind of sample	Mn obtained by bismuthate method (%)	Mn obtained by this method (%)	Difference (%)
Fe-Mn	75.34	$\left.\begin{array}{l}75.36\\75.73\\75.57\end{array}\right\}75.55$	+0.21
Fe-Mn	76.24	$\left.\begin{array}{l}76.18\\76.20\\76.02\end{array}\right\}76.13$	−0.11
Fe-Mn	77.42	$\left.\begin{array}{l}77.53\\77.82\\77.64\end{array}\right\}77.66$	+0.24

Summary

(1) Determination of manganese by oxidation with ammonium persulfate and reduction with the excess of ferrous sulfate and then back titration with potassium permanganate was examined from various angles and the following results were obtained.

(2) On the relationship between the amount of manganese and the requisite amount of phosphoric acid, larger amount of phosphoric acid was necessary with increase in the manganese content, with about 2 g of ammonium persulfate and a total volume of 200 ml, while the amount of phosphoric acid necessary was smaller with 8 g of ammonium persulfate and a total volume of 400 ml.

(3) Regarding the concentration of the acid, approximately 1.4~2.0N of sulfuric acid or 0.6~1.0N of sulfuric and nitric acid (3 : 1) mixture gave quantitative results when 4 g of ammonium persulfate was used in a total volume of 400 ml. When 8 g of the persulfate was used, 1.5~2.0N of sulfuric acid solution or 1.0~1.2N of sulfuric and nitric acid (3 : 1) mixture was found to give satisfactory results, showing that the determinable range is comparatively narrowed than in the case of using 4 g of ammonium persulfate.

(4) Boiling for 1~5 minutes after the large bubbles began to appear gave quantitative results while a somewhat lower values were obtained when boiled more than 6 minutes.

(5) Summarizing the foregoing results, a suitable analytical procedures for the determination of manganese in ferromanganese were proposed and results obtained by some samples by this method were shown.