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# Volumetric Determination of Manganese after Oxidation by Periodate<sup>1</sup>

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Manganese up to 30 mg. can be determined by oxidation to permanganate with periodate in either phosphoric or sulfuric acid solution, removal of excess periodate by precipitation as mercuric salt, and reduction of the permanganate by standard ferrous sulfate. The reaction goes best in a phosphoric acid solution, in which case less than a milligram of chromium does not interfere. Cobalt, cerium, and chloride must be absent.

WILLARD and Greathouse (4) have shown that manganese can be determined colorimetrically by oxidation to permanganate with a small excess of periodate. The solution thus obtained is stable for weeks, a fact confirmed by others (3). It seemed desirable, therefore, to make this the basis of a volumetric method by removing the excess of periodate. This was accomplished by precipitation as mercuric periodate, after which the permanganate was titrated by adding excess of standard ferrous sulfate and back titrating with permanganate. Although bismuth periodate is the least soluble of all, its presence caused certain errors which made its use for this purpose impossible.

<sup>1</sup> Received August 12, 1931. Presented before the Division of Physical and Inorganic Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

<sup>2</sup> From a dissertation submitted by J. J. Thompson to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of doctor of philosophy.

### Precipitation of Periodate as Bismuth Salt

A known volume of standard permanganate was reduced with ferrous sulfate in a dilute sulfuric acid solution, and the manganous salt was then oxidized to permanganate by adding 0.3 gram of sodium metaperiodate,  $\text{NaIO}_4$ , and boiling gently for 15 minutes. After cooling to room temperature, the excess periodate was precipitated by the addition of bismuth perchlorate, as a white, voluminous precipitate of bismuth periodate. The solution was immediately titrated with standard ferrous sulfate. To make the end point more distinct in the presence of the precipitate, alphasurine (Erioglaurine A) (2) was added just before the end point. Too little ferrous sulfate was always used, showing that some permanganate had been reduced, because other experiments proved that oxidation was complete. The surprising fact was that in the presence of iodate some of the permanganate was used in the oxidation of bismuth. In the presence of bismuth periodate only, no such error occurred. Both bismuth and iodate are necessarily present because the latter is formed by reduction of the periodate by manganous ion (4). It could not be completely removed by precipitation as silver iodate. If standard permanganate to which as much as 0.6 gram of sodium periodate had been added was treated with a bismuth salt, and, without filtering, titrated with ferrous sulfate, accurate results were obtained. If, however, excess of the latter was added and back titrated with permanganate, the results indicated that the excess of ferrous salt was slowly oxidized by the precipitate of bismuth periodate even in cold solution.

There are, therefore, two errors to be considered: oxidation of the excess reducing agent by iodate or insoluble bismuth periodate, and oxidation of bismuth. Of the possible volumetric reducing agents, vanadyl sulfate and ferrous sulfate were slowly oxidized by bismuth periodate, but oxalate and hydrogen peroxide were not affected. On the other hand, the former were not oxidized by the low concentration of iodate, but the two latter were oxidized. The use of bismuth as a precipitant, therefore, had to be abandoned.

### Precipitation of Periodate as Mercuric Salt

It was found that periodate could be completely precipitated as the mercuric salt,  $\text{Hg}_5(\text{IO}_6)_2$  (5). Although more soluble than the bismuth salt, it is still sufficiently insoluble even in the concentration of acid used for the oxidation of manganese, provided a large excess of mercuric ion is present. The mercuric salt has a very decided advantage in that it is much more easily filtered. There is also no possibility of further oxidation of the mercury by permanganate. Experiments showed that amounts of manganese up to 30 mg. could be accurately determined by oxidation to permanganate in a solution containing either phosphoric, sulfuric, or phos-

phoric and sulfuric acids. There was no blank correction to be applied. In this respect there is a slight advantage over the bismuthate method (1). Iron ores can be quickly dissolved in phosphoric acid<sup>3</sup> and this method applied directly to the solution, but this is not possible with bismuthate.

Table I—Effect of Chromium on Determination of Manganese

MATERIAL USED	ACID PRESENT	AP-PROX. CHROMIUM		MANGANESE	
		WT. OF SAMPLE	PRESENT	Present	Found
		Grams	Mg.	%	%
B. S. Steel, No. 10c	Phosphoric	1.1	4.0	1.13	1.160
B. S. Steel, No. 10c	Phosphoric	1.0	3.0	1.13	1.153
B. S. Steel, No. 10c	Phosphoric	1.0	2.0	1.13	1.148
B. S. Steel, No. 10c	Sulfuric	1.3	2.0	1.13	1.232
B. S. Steel, No. 10c	Phosphoric	1.0	1.5	1.13	1.143
B. S. Steel, No. 10c	Phosphoric	1.0	1.0	1.13	1.138
B. S. Steel, No. 10c	Phosphoric	1.0	0.5	1.13	1.139
B. S. CrNi Steel, No. 32b	Phosphoric	1.14	7.3	0.624	0.661
B. S. CrNi Steel, No. 32b	Phosphoric	1.04	6.6	0.624	0.664
B. S. CrNi Steel, No. 32b	Phosphoric	1.18	7.6	0.624	0.749
B. S. CrNi Steel, No. 32b	Phosphoric	1.20	7.7	0.624	0.686

Experiments using standard permanganate were carried out to determine the accuracy of the method. Samples of 25 to 40 cc. of 0.05 *N* permanganate were reduced with ferrous sulfate in a solution containing, in a volume of 100 cc., about 10 to 15 cc. of 85 per cent phosphoric acid, or mixtures of 3 or 4 cc. of phosphoric acid with 5 or 4 cc. of concentrated sulfuric acid, and oxidized by adding 0.3 to 0.5 gram of sodium or potassium periodate and heating just to boiling for 15 minutes. The solution was cooled to room temperature, diluted to 150 cc., and 2 to 5 grams of mercuric nitrate,  $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , dissolved in a little water, were added to precipitate the excess periodate and nearly all of the iodate. The solution was filtered into an excess of 0.05 *N* ferrous sulfate through an asbestos mat 3 to 4 mm. thick on a 9-cm. No. 17G sintered-glass filtering funnel. A Büchner funnel would doubtless be almost as satisfactory. The precipitate of mercuric periodate was washed four times with water, and the excess of ferrous sulfate was titrated back with standard permanganate. The results obtained were the same within 0.01 cc. as in the direct titration of the ferrous sulfate with permanganate. When chromium was present, it was found that in the presence of sulfuric acid about 60 per cent of it was oxidized when the content was about 1.5 mg., thereby giving high results for manganese. However, this tendency is very much minimized in phosphoric acid solutions, so that an accurate determination of manganese can be made in the presence of 1 mg. of chromium. Because of the difficulty in washing out all the permanganic acid from very large precipitates of mercuric periodate, only 0.3 gram of sodium or potassium periodate should be used for 15 mg. or less of manganese. Accurate results can be obtained, however, with as much as 30 mg. of manganese, using, in this case, 0.5 gram of periodate. With

<sup>3</sup> Unpublished work by one of the authors.

larger amounts such voluminous precipitates are formed that all the permanganic acid cannot be removed by washing. Instead of the metaperiodate, the paraperiodate,  $\text{Na}_3\text{H}_2\text{IO}_6$ , may be used. Manganese is more readily oxidized and the permanganic acid formed is more stable in a phosphoric acid solution, so that this acid is desirable when considerable amounts of manganese are present.

The concentration of acid may vary within wide limits as far as oxidation of manganese is concerned, although with large amounts of the latter, manganese dioxide may form unless phosphoric acid is present. A fairly high concentration of acid increases the rate of oxidation. The solubility of mercuric periodate, however, is increased under these conditions, so that it is advisable to dilute the solution before removing the excess of periodate. Concentrations not greater than 5 cc. of sulfuric acid, sp. gr. 1.83, or 15 cc. of 85 per cent phosphoric acid per 100 cc. are recommended. Mixtures of the two acids are desirable, because the mercuric periodate is more crystalline in the presence of sulfuric acid, and without some phosphoric acid, manganese dioxide may form.

The weight of mercuric nitrate required for complete precipitation of periodate varies from 5 grams with 5 cc. of sulfuric acid to 2 grams with 15 cc. of phosphoric acid per 100 cc.

Titration of the permanganic acid with arsenite instead of ferrous sulfate is impossible because of an indefinite end point.

Chloride must be absent. Cobalt interferes as in the bismuthate method (1). When periodate is added to a solution of cobaltous sulfate, the solution becomes dark brown, owing to oxidation of the cobaltous salt. In steel containing 1.13 per cent of manganese and 0.5 per cent of cobalt, 1.32 per cent of manganese was obtained. Cerium also interferes because it is oxidized to a ceric salt.

#### Procedure for Steel or Iron Free from Chromium

Dissolve 1 gram of steel containing not more than 0.15 mg. of chromium in 4 cc. of concentrated sulfuric acid and 25 cc. of water. To the hot solution, add, cautiously, 1 cc. or more of concentrated nitric acid to oxidize the ferrous iron and carbonaceous matter, and boil to remove nitrous fumes. Any graphite present will do no harm and will be filtered out later. Dilute to 50 or 75 cc., add 3 cc. of 85 per cent phosphoric acid (or an equivalent amount of more dilute acid) and 0.3 gram of sodium or potassium periodate. Boil gently for 15 minutes to oxidize the manganese, dilute to 150 cc., cool to room temperature, and add slowly, with constant stirring, 4 or 5 grams of mercuric nitrate ( $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ) dissolved in a little water. Filter immediately through a fairly large asbestos filter into an excess of standard

ferrous sulfate, wash with cold water four or five times, and titrate back with standard permanganate.

#### Procedure for Steel or Iron Containing Not Over 0.1 Per Cent of Chromium

Dissolve 1 gram in a mixture of 15 cc. of water and 15 cc. of 85 per cent phosphoric acid. Oxidize the ferrous iron and carbonaceous matter by adding carefully to the hot solution 1 or 2 cc. of concentrated nitric acid, and boil to remove nitrous fumes. Dilute to 100 cc., add 0.3 gram of sodium or potassium periodate, boil gently 15 minutes to oxidize the manganese, dilute to 150 cc., and cool to room temperature. Precipitate the periodate by adding slowly, with constant stirring, 2 to 3 grams of mercuric nitrate dissolved in a little water, and filter immediately through a fairly large asbestos filter into excess of standard ferrous sulfate containing 10 cc. of 50 per cent sulfuric acid to prevent precipitation of mercuric phosphate. Wash with cold water four or five times and titrate back the filtrate and washings with standard permanganate. The filtration will be slower than when sulfuric acid is present during precipitation, but the time required, including washing, should not be more than 3 minutes. The effect of chromium with and without phosphoric acid is shown in Table I.

#### Procedure for Iron Ore and Other Oxide Ores

Place 1 gram in a 250-cc. Pyrex beaker, and add 15 cc. of 85 per cent phosphoric acid and a few drops of concentrated sulfuric acid. Stir until all the ore is free from the bottom of the beaker, cover, and heat until fumes of sulfuric acid are given off, taking care that it does not froth over or cake on the bottom. If the ore is not dissolved by this time, keep it hot for a longer time, stirring occasionally, but not allowing the temperature to rise, because the beaker would be attacked. Cool until the mass begins to be viscous, then add quickly 100 cc. of water, and heat. Everything should dissolve except some gelatinous silica. From here on the procedure is the same as for steel containing 0.1 per cent of chromium.

#### Procedure for Bronze

Dissolve 1 gram in a mixture of 3 cc. of concentrated nitric acid, 10 cc. of 85 per cent phosphoric acid, and about 7 or 8 cc. of water. Then dilute to 50 or 75 cc. and proceed as above. Owing to the deep blue color of the copper salt, the back titration with permanganate is conveniently carried out electrometrically or by use of alphasurine indicator (2).

*Note*—If the amount of manganese is between 15 and 30 mg., the amount of periodate in the above procedures should be increased to 0.5 gram.

Results obtained by this method with different materials are shown in Table II. In all cases phosphoric acid was

used with the sulfuric to prevent formation of manganese dioxide.

Table II—Determination of Manganese in Various Materials

MATERIAL ANALYZED	ACID USED	AF-PROX. CHRO-		MANGANESE	
		WT. OF SAMPLE	PRES-ENT	Present Found	
				Grams	%
B. S. Steel, No. 10c	Phosphoric	1.06	0.01	1.13	1.136
B. S. Steel, No. 10c	Phosphoric	1.03	0.01	1.13	1.132
B. S. Steel, No. 10c	Sulfuric	1.29	0.01	1.13	1.138
B. S. Steel, No. 10c	Sulfuric	1.01	0.01	1.13	1.139
B. S. Cast Iron, No. 4c	Phosphoric	1.04	0.016	0.897	0.890
B. S. Cast Iron, No. 4c	Phosphoric	1.18	0.016	0.897	0.894
B. S. Cast Iron, No. 4c	Sulfuric	1.14	0.016	0.897	0.898
B. S. Cast Iron, No. 4c	Sulfuric	1.13	0.016	0.897	0.912
B. S. Steel, No. 21b	Phosphoric	1.26	0.021	0.564	0.570
B. S. Steel, No. 21b	Phosphoric	1.12	0.021	0.564	0.562
B. S. Steel, No. 16b	Phosphoric	1.10	0.007	0.381	0.389
B. S. Steel, No. 16b	Phosphoric	1.24	0.007	0.381	0.388
B. S. Steel, No. 16b	Sulfuric	1.02	0.007	0.381	0.390
B. S. Steel, No. 16b	Sulfuric	1.22 <sup>a</sup>	0.007	0.381	0.392
Steel A	Phosphoric	1.47 <sup>a</sup>	0.065	1.99	1.99
Steel A	Phosphoric	1.46 <sup>a</sup>	0.065	1.99	1.98
Steel A	Sulfuric	0.49	0.065	1.99	2.02
Steel A	Sulfuric	0.43	0.065	1.99	2.00
B. S. Mn Bronze, No. 62	Phosphoric	0.69	...	1.59	1.61
B. S. Mn Bronze, No. 62	Phosphoric	0.62	...	1.59	1.64
B. S. Norrie Iron Ore, No. 28	Phosphoric	1.00	...	0.465	0.446
B. S. Norrie Iron Ore, No. 28	Phosphoric	1.09	...	0.465	0.447
B. S. Bauxite, No. 69	Phosphoric	1.27	...	0.426	0.421
B. S. Bauxite, No. 69	Phosphoric	1.26	...	0.426	0.420

<sup>a</sup> These samples contain nearly 30 mg. of manganese.

#### Literature Cited

- (1) Hillebrand and Lundell, "Applied Inorganic Analysis," p. 345, Wiley, 1929.
- (2) Knop, *Z. anal. Chem.*, **77**, 125 (1929).
- (3) Richards, *Analyst*, **55**, 554 (1930).
- (4) Willard and Greathouse, *J. Am. Chem. Soc.*, **39**, 2366 (1917).
- (5) Willard and Thompson, *IND. ENG. CHEM., Anal. Ed.*, **3**, 398 (1931).

