*The Volumetric Determination of Manganese in Ores**

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An improved method has been needed for the determination of moderate amounts of manganese in minerals, ores, and metals. Many methods which are applicable to small amounts of manganese cannot be accurately applied to substances containing high concentrations of manganese.

Of the many methods which have been published concerning the determination of manganese, few exist which do not have serious shortcomings. The method where manganese is oxidized to permanganate with sodium bismuthate[1,2] is time-consuming and requires filtration through a substance which does not reduce permangante, and the danger exists that the solution will come into contact with reducing substances. This method is generally applied to low concentrations of manganese. Cerium and cobalt are known to interfere, and chromium requires special attention. The method in which manganese is oxidized to permanganate with peroxysulfate and titrated with arsenite[3] often gives trouble with the end-point detection because of the reoxidation of manganese by the residual peroxysulfate. As with the bismuthate method, this method is generally applied to small amounts of manganese. The direct Volhard titration method with permanganate[1] is attended with great difficulty since manganese(IV) oxide precipitates and imparts a brown color to the solution which partially obscures the end point. The chelatometric titration of manganese with a solution of ethylenediaminetetraacetic acid (EDTA)[4] is non-specific and requires the presence of masking agents and a careful control of the pH values.

Schroder[5] found that manganese is quantitatively converted to manganese(III) from any valence state by heating solutions containing manganese to fumes with a mixture of perchloric and phosphoric acids; he applied this process to the determination of manganese in ferromanganese, steel, and brass by titrating the manganese(III) with a ferrous solution. He also applied the method to the photometric determination of manganese in aluminum alloys,[6] by measuring the intensity of the redish color of the manganese(III) ion. The process was applied by Nagato[7] to the photometric determination of manganese in ferrite. When possible reagents were investigated by Kitakawa and Shibata[8] for the quantitative conversion of manganese to manganese(III), they reported that a mixture of phosphoric acid and sodium bismuthate was also effective for this purpose. Kimura, Tanino, and Kitahara[9] treated various samples containing manganese(IV) oxide with a mixture of phosphoric and sulfuric acids and titrated the resulting manganese(III) with a ferrous solution; however, this process is applicable only to samples containing manganese chiefly as manganese(IV) oxide.

Several methods which appeared to offer the greatest probability of successful application were tested in this laboratory. The method whereby manganese is oxidized to manganese(III) using the phosphoric acid-perchloric acid system seemed attractive because of its simplicity. The applicability of this method to large amounts of manganese is evident since the reduction of manganese(III) to manganese (II) involves a valence change of one, whereas methods in which manganese is oxidized to permanganate and reduced to the manganous ion involves a valence change of five.

It was found that manganese(III) can be kept in the concentrated acid mixture for several days without any noticeable reduction, but if the solution is diluted, titration should follow within a few hours.

The only interference encountered with the method was titanium in excess of 30 mg. It was found that titanium in excess of this amount precipitated as an insoluble phosphate

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1) "Japanese Industrial Standards," M8236 (1953), M8236 (1958).

2) "Methods For The Chemical Analysis of Metals," A. S. T. M. 1950, pp., 80, 82, 150.

3) "Methods For The Chemical Analysis of Metals," A. S. T. M., 1950, p. 150.

4) K. Watanuki and S. Tomura, *Japan Analyst*, **10**, 1027 (1961); see also H. Flaschka, *Chemist-Analyst*, **42**, 56 (1958).

5) H. Schroder, *Metall*, 8, 542 (1954).

6) Idem., ibid., **9**, 100 (1955).

7) H. Nagato, *Japan Analyst*, **10**, 985, 991 (1961); **11**, 1291 (1962).

8) K. Kitakawa and N. Shibata, *Japan Analyst*, **9**, 597 (1960).

9) K. Kimura, K. Tanino and S. Kitahara, *Rikagaku Kenkyusho Hokoku*, 229 (1959).

TABLE I. DETERMINATION OF MANGANESE IN VARIOUS MIXTURES

	Sample	Mn added mg.	Mn recovered mg.
1) a)	100 mg. of Mn-oxide ore+100 mg. of pyrite	55.00	55.12
b)	100 mg. of Mn-oxide ore+100 mg. quartz	55.00	55.09
c)	100 mg. of Mn-oxide ore+100 mg. zinc blend	55.00	55.31
2) a)	$KMnO_4$ solution+200 mg. Chromium	54.90	55.55
b)	$KMnO_4$ solution+200 mg. Chromium	54.90	55.23
c)	$KMnO_4$ solution+200 mg. Vanadium	54.90	55.11
3) a)	$KMnO_4$ solution+5 ml. H_2SO_4	54.90	54.95
b)	$KMnO_4$ solution+3 g. Na_2SO_4	54.90	55.22
c)	$KMnO_4$ solution+10 g. K_2SO_4	54.90	—

(1) Manganese oxide ore is the mixture shown in annotation (2) of Table II, average of two determinations.
(2) a) Chromium added as $(NH_4)_2CrO_4$, (2) b) Chromium added as $Cr_2(SO_4)_3$, (2) c) Vanadium added as $VOCl_2$.
(3) c) Upon dilution with water, a considerable amount of K_3PO_4 precipitated and some manganese was retained by the precipitate.

TABLE II. RESULTS OF ANALYSIS

	Sample	Weight of sample, mg.	Mn found %	Mn by other methods, %
(1)	Ferromanganese	100	75.11	75.3*
		200	74.98	
(2)	Mn-oxide ore	100	55.09	55.08
		200	54.91	
(3)	Mn-carbonate ore	100	36.33	36.45
		200	36.41	
(4)	Mn-silicate ore (a)	200	27.03	27.06
		500	27.06	
	(b)	200	31.55	31.78
		300	31.76	
	(c)	200	49.88	49.35
		200	49.03	

(1) Recommended value*: Japanese Standard ferromanganese sample No. 13A.
(2) Mixture of pyrochroite $Mn(OH)_2$ and Hydrohausmannite $(Mn^{2+}, Mn^{3+})(OH,O)_2$ from Noda-Tamagawa mine, Iwate Prefecture, Japan.
(3) Calcian rhodochrosite $(Mn, Ca)CO_3$ from Teine mine, Hokkaido, Japan.
(4) (a) Bustamite $(Mn, Ca)SiO_3$ from Kanoiri mine, Tochigi Prefecture, Japan.
(b) Pyroxmangite $(Mn, Fe)SiO_3$ from Kaso mine, Tochigi Prefecture, Japan.
(c) Tephroite Mn_2SiO_4 from Kanoiri mine, Tochigi Prefecture, Japan

and co-precipitated some manganese. The separation of 25 mg. of manganese from 200 mg. of titanium was carried out by means of the addition of sodium peroxide to a nearly neutral solution, followed by the filtration of the precipitated manganese dioxide.[10] Quantities of manganese in excess of 25 mg. interfered by causing a rapid decomposition of the peroxide, which resulted in the precipitation of a considerable quantity of titanium.

Manganese ores often contain sulfide minerals such as pyrite (FeS_2). It was found that these minerals dissolve readily in the acid mixture used in the procedure and cause no interference. Up to 5 ml. of sulfuric acid in the acid mixture is without effect, and the presence of up to 3 g. of potassium sulfate causes no interference, but more than 5 g. of potassium sulfate caused bad results because of the precipitation of potassium phosphate upon dilution, which co-precipitated some manganese. The presence of 5 g. of sodium sulfate caused difficulty with some samples because of the insolubility of the mixture, which solidifies upon cooling.

The effects of chromium and vanadium upon the determination were investigated. Chromium imparts a color to the solution which makes the end point difficult to detect. The addition of a ferrous *o*-phenanthroline indicator effectively eliminates any interference from

10) M. Codell, "Analytical Chemistry of Titanium Metals and Compounds," Interscience-Wiley, New York (1959), p. 172.

this source, however. Vanadium is converted to vanadium(V) upon fuming with the acid mixture and consumes the ferrous solution upon titration. In the presence of vanadium, it is, therefore, necessary to add an excess of ferrous solution and back-titrate with a permanganate solution. Vanadium(V) is reduced to vanadium(IV) by the ferrous solution and oxidized to vanadium(V) by the permanganate solution; the net result is the same.

Table I shows the recovery of manganese from various ores to which known amounts of manganese have been added, and from solutions of permanganate to which substances have been added to determine their possible interference with the quantitative recovery of manganese.

Table II gives an analysis, by the proposed method, of ferromanganese and ores which have been previously analyzed for manganese content by other methods.

The following procedure and the two modified procedures should provide a means of analyzing most substances containing moderate amounts of manganese which are likely to be encountered.

Experimental

A Procedure for Samples Other than Silicate Ores and Containing Less than 30 mg. of Titanium.—Transfer a sample to a 300 ml. conical beaker. Add 5 ml. of water to moisten the sample, and, if the presence of organic matter is suspected, add 5 ml. of concentrated nitric acid. Add 10 ml. of phosphoric acid and 10 ml. of perchloric acid. Warm gently on a hot plate. If the sample does not dissolve, add 5 ml. of hydrochloric acid and heat gently. If the sample still remains undissolved, remove from heat and add 5 ml. of 10% hydrogen peroxide. Heat strongly until fumes of perchloric acid issue freely from the top of the beaker. Remove from the hot plate and allow to cool. Add 200 ml. of water and titrate with a 0.1 N ferrous ammonium sulfate solution until the red color disappears.

For samples containing chromium in quantities sufficient to cause a deep color, add 4 drops of a ferrous *o*-phenanthroline indicator to enable the end point to be detected.

For samples containing vanadium, add an excess of a ferrous ammonium sulfate solution and 4 drops of a ferrous *o*-phenanthroline indicator and back-titrate with a 0.1 N potassium permanganate solution.

Procedure for Silicate Ores.—Place the sample in a platinum dish, moisten with water, and 10 ml. of perchloric acid and 10 ml. of concentrated hydrofluoric acid. Evaporate to strong fumes of perchloric acid. Cool, transfer the solution to a conical beaker, and proceed as directed above.

Procedure for Samples Containing up to 200 mg. of Titanium and not more than 25 mg. of Manganese.—Dissolve the sample with hydrochloric acid, with a mixture of hydrochloric and hydrofluoric acids, or by fusion with 3 g. of sodium bisulfate with a few drops of sulfuric acid. If alkali fusion has been used, render the solution slightly acid with hydrochloric acid. To the acidic solution of the sample, add 20% sodium hydroxide until the first permanent precipitate forms; then add 3 g. of sodium peroxide and heat gently until it boils. Allow to cool to about 60°C and, if some titanium appears to have precipitated, add 5 ml. of 10% hydrogen peroxide. Filter through a rapid paper and wash the precipitate with a 1% solution of sodium carbonate containing 1% hydrogen peroxide. Discard the precipitate.

To the filtrate add 10 ml. of phosphoric acid and 10 ml. of perchloric acid and proceed as directed under the first procedure.

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