SÄRNSTRÖM'S METHOD OF DETERMINING MANGANESE IN IRON ORES.

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ABOUT a year ago we had occasion to use a volumetric method which would allow the determination of manganese in iron ores ranging in amounts up to fifteen per cent. and give results in half an hour which would check with gravimetric determinations within two-tenths per cent. for ores as high as fifteen per cent., and within a few hundredths of a per cent. for ores under one per cent.

We found in use in a neighboring laboratory a method which was generally known as the "Swedish Method." This method was found to fulfill the above conditions, and seems to have sufficient merit to be more widely known.

The first suggestion upon which the method is based was made by Guyard,[1] although his method of operating it did not give very satisfactory results.

The first description of the method in its present practicable form, was made by C. G. Särnström, in the Jernkontorets Annaler, (Sweden), 1881, p. 401.[2]

The principle upon which this method depends, is the reaction which takes place when a manganese compound higher in oxygen than the manganous state, is dissolved in hydrochloric acid, forming a higher chloride, which is readily shown by the dark colored solution. When this solution is boiled, it rapidly decolorizes, being completely converted into manganous chloride, not easily oxidized by the air while in the acid solution.

In neutral or alkaline solutions the manganous compound has a slight tendency to oxidize in contact with the air, but we have never detected any appreciable oxidation under the conditions which we follow.

The separation of the iron and the manganese is effected in

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[1] Guyard: *Chem News*, 8, 292; the following references relate to the subsequent modifications of the method; Habich: *Ztschr. anal. Chem.*, 3, 474; Winkler: *Ztschr. anal. Chem.*, 3, 423; Morawski und Stingl; *J. prakt. Chem.* (N. F.), 18, 96; Volhard: *Ann. Chem.* (Liebig), 198, 318.

[2] Also published in Berg und Hüttenm. *Zeitung*, 40, 425. A review of the original article appears in the *Ztschr. anal. Chem.*, 22, 84. We are indebted to Mr. Hugo Carlsson, Chief Chemist of the Johnson Works of Lorain, Ohio, for calling our attention to Särnström's original publication and for furnishing us a translation of the same.

such a way that the iron is precipitated as hydroxide and the manganese left in the manganous condition in solution. Sodium carbonate is used to precipitate the iron as hydroxide and no trouble is experienced in the precipitation of the manganese as a carbonate, provided that only a very slight excess is employed beyond that necessary to completely precipitate the iron. It is advisable to add the sodium carbonate in the form of a solution, towards the completion of the precipitation of the iron, to avoid such an excess.

Särnström employs sodium bicarbonate, which has the advantage that a greater amount of carbon dioxide is generated, preventing subsequent oxidation of the manganous salt by the oxygen of the air. Manganese bicarbonate is formed, which is readily soluble in the solution containing carbon dioxide.

It is always desirable to test the sodium carbonate or bicarbonate for organic matter.

The results given below show the necessity of avoiding an excess of sodium carbonate (the same is true of the bicarbonate) in the precipitation of the iron. Aliquot portions of a solution of manganese containing 3.14 per cent. manganese gravimetrically determined, gave only 2.61 per cent. when treated with such an excess. Another ore giving 8.69 per cent. under the proper conditions of this method, when treated with an excess of sodium carbonate gave 5.38 per cent.

After the precipitation of the iron in the hot solution, the manganese being in the manganous state, is oxidized by potassium permanganate, according to the following formula,

$$3MnO + 2KMnO_4 + H_2O = 2KOH + 5MnO_2,$$

which is the same reaction which takes place in Volhard's method. As the titration takes place directly, without filtering, the precipitate of ferric hydroxide is an advantage, especially in low manganese ores, as it serves to collect the fine precipitate of manganese dioxide and causes it to settle more rapidly.

In ores very low in iron, it is desirable to add ferric chloride in order to obtain the requisite amount of the iron precipitate.

The Method.—Weigh half a gram ore into a No. 0 beaker, add fifteen cc. of hydrochloric acid, 1.1 sp. gr., and boil until the residue is clear. If necessary fuse the residue with sodium carbonate. Add a few drops of nitric acid to oxidize any ferfous iron or organic matter. In magnetic ores more of course will be necessary. It is well to test for ferrous iron. Evaporate a short time to expel any nitrous acid that may have been formed. It is advisable to have a good amount of free hydrochloric acid present to generate carbon dioxide in the precipitation with sodium carbonate. The solution is then washed into a No. 3 beaker or a flask, which is then filled about two-thirds full with boiling, distilled water and solid sodium carbonate or bicarbonate added until the iron is completely precipitated, which is readily indicated by the characteristic spongy appearance of the precipitated ferric hydroxide. A solution of the salt is preferable for the final precipitation in order to avoid an excess.

The solution should be about 80° C. when it is titrated[1] with potassium permanganate directly, without filtering, and with intervals of vigorous stirring and settling of the iron and manganese precipitates, until the supernatant liquid shows a permanent faint pink color. The first appearance of the pink color must not be taken as an indication that the oxidation is complete, as gentle heating and vigorous stirring will allow more potassium permanganate to be added before the permanent pink appears.[2]

Multiplying the burette reading by two represents the equivalent for one gram, and this multiplied by the permanganate value in manganese, which is the iron value multiplied by 0.2946, gives the percentage of manganese.

In case of overtitration, it is practicable to titrate back with a carefully standardized solution of manganous chloride, which is prepared by evaporating fifteen cc. potassium permanganate down to three or four cc., adding a few drops of hydrochloric acid and boiling as long as chlorine comes off. The solution should be neutralized with sodium carbonate and diluted to ten cc., when one cc. is equal to one cc. of potassium permanganate.

Särnström states that the method is reliable for high manga-

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[1] Which should be done immediately after the neutralization, in order to avoid any opportunity for oxidation.

[2] This is a very important point not only in relation to this method, but in all methods where potassium permanganate is used.

nese ores and ferro-manganese "where it is not necessary to determine the manganese closer than a few tenths of one per cent."

Our experience does not confirm this. The results average from one to two per cent. too low, so that we do not consider the method at all reliable for high percentages of manganese.

The following are some results which show this :

	Särnström. Per cent.	Gravimetric (Ford's.) Per cent.
Illinois Ore	52.06 (1)	52.98
	51.91 (2)	....
	51.40 (3)	....
	51.78 (4)	....
	51.37 (5)	....
	51.37 (6)	....
No. 595	42.07	....
	42.35	44.3
	42.90	....
	42.60	....

In analyses from No. 1 to No. 4 sodium carbonate was used for the precipitation. To determine whether the employment of sodium bicarbonate would be advantageous, No. 6 was so treated while at the same time No. 5 was precipitated with sodium carbonate, yielding the same result. We have tried sodium bicarbonate with low manganese ores, but have never noticed any practical advantages, while theoretically, as we have pointed out above, there should be an advantage in the employment of sodium bicarbonate.

This discrepancy with high percentages of manganese may possibly be accounted for, by the fact that the large precipitate of manganese dioxide may act in a purely mechanical way in protecting the final amounts of the manganous chloride from being fully oxidized to dioxide by the potassium permanganate. It is to be noted in this connection that Volhard's method does not generally give reliable results with such high percentages of manganese.

The following are some results obtained by this and other methods :

	Särnström.	Volhard.	Gravimetric.
A. Magnetic	0.07	0.10	0.07
Specular	...	0.08[1]	...
B. Mixture of blue granular and red hematite.	0.30	0.31	0.29
	0.32	0.29	0.30
	0.28	...	...
C. Limonite	1.03	1.02	1.09
	1.05	1.05	...
D. Silicious ore	2.98	3.08	2.93
	3.07	3.07	...
Cary Empire	3.93	T. V. Church	3.94
	3.88	Illinois Steel Co	
Dexter No. 2	6.04	...	...
	6.02	6.02	6.01
	6.01	...	...
Davis ore	8.78	8.62	8.86
		A. G. McKenna,	(Ford's)
Newark ore	1.48	Duquesne Steel Works,	1.50
No. 57	5.39	5.39	...
No. 218	5.59	5.59	...

In the determination of small amounts of manganese this method presents an advantage over Volhard's method in giving a more distinct end reaction.

The method can be used for iron and steel determinations if the usual precautions are taken to oxidize the carbon. But it is not so well adapted to these on account of the impracticability of taking large amounts for analysis.

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ON VARIOUS MODIFICATIONS OF THE PEMBERTON VOLUMETRIC METHOD FOR DETERMINING PHOSPHORIC ACID IN COMMERCIAL FERTILIZERS.

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IF an excuse is needed for adding to the already voluminous literature on the method as proposed by Pemberton[2] and modified by Kilgore, it is found[3] in the action taken by the Association of Official Agricultural Chemists at their last meeting. The method, as modified by Kilgore, gave almost uniformly excellent results on known solutions, in a two years trial in the hands of a number of analysts, and only failed to become

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[1] This was so low as to necessitate filtering through asbestos in order to see end reaction by Volhard's method.

[2] This Journal, 15, 382.

[3] Bul. 43, Div. Chem. U. S. Dept. Agr., 104.