DETERMINATION OF MANGANESE IN IRON.[1]

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THE process here described involves no new principle. It is a combination of several different processes and, so far as we are aware, has not been used before.

REAGENTS.

Ferrous Ammonium Sulphate.—Dissolve 8.56 grams crystallized ferrous ammonium sulphate in water containing 40 cc. of dilute sulphuric acid (25 per cent.), and make to 1 liter.

Potassium Permanganate.—A standard solution of such strength that 1 cc. is equivalent to about 0.001 gram iron. The manganese equivalent for the present method is found by multiplying the iron equivalent by $^{55}/_{112}$.

Sodium Acetate.—Thirty grams of crystallized sodium acetate, 30 cc. of acetic acid (30 per cent.), and 170 cc. of water.

Bromine Water.—A saturated solution.

Dissolve 1.5 grams of the sample in 25 cc. of nitric acid (sp. gr. 1.20), or in 20 cc. of nitric acid and 5 cc. of hydrochloric acid, (sp. gr. 1.12). Heat till dissolved, transfer to a 300 cc. flask, add a solution of sodium carbonate till nearly neutral, and then an emulsion of zinc oxide slowly till the precipitate of ferric hydroxide forms. After two minutes add an excess of zinc oxide.[2] Make up the volume to 300 cc., mix by pouring back and forth into a dry beaker, and filter through a dry filter.

Take 200 cc. of the filtrate, add 20 cc. of the solution of sodium acetate and 40 cc. of bromine water. Heat nearly to boiling, stirring occasionally and adding more bromine water, if necessary, till the precipitate of manganese dioxide separates. Filter and wash. The precipitate adhering to the beaker need not be removed, but the beaker must be rinsed thoroughly. Place the beaker under the funnel containing the precipitate and drop upon the latter, from a burette, the solution of ferrous ammonium sulphate till solution is complete. During this operation break up the precipitate occasionally with a fine stream of water from a wash-bottle. Unless the manganese exceeds 0.4 per cent., not more than 20 cc. of the solution should be used.

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[1] The work here described formed the basis of a thesis for the degree of Bachelor of Science at the Rose Polytechnic Institute.

[2] Geo. Auchy: This Journal, **18**, 998.

Wash out the filter and titrate the filtrate with the standard permanganate solution. The difference between the number of cubic centimeters of permanganate used and the amount which would have been used by the ferrous ammonium sulphate employed, if no manganese dioxide had been dissolved in it, multiplied by the manganese equivalent of the solution, will give the amount of manganese in 1 gram of iron.

In testing the method, considerable difficulty was experienced in obtaining an iron solution free from manganese. All samples of ferrous sulphate and of iron ores which were available contained some of that element. Finally it was found that a sample of ammonia iron alum was free from manganese and by precipitating a solution of the salt with sodium hydroxide, washing by decantation, and dissolving in sulphuric acid a ferric sulphate solution free from manganese was prepared. A manganese solution of known strength was prepared by dissolving a weighed quantity of potassium permanganate in water, just decolorizing with sulphurous acid and making up to a known volume. A quantity of the iron solution containing 1.5 grams of iron was mixed with a measured quantity of the manganese solution and the manganese was determined by the process described above. The results were as follows, stated as per cents. of the iron present.

Manganese taken.	Manganese found.
0.100	0.109
0.300	0.300
0.300	0.300
0.500	0.490
0.700	0.687
0.700	0.681
0.900	0.897
1.100	1.090

To determine whether evaporation with sulphuric acid to expel the nitric acid used for solution, as is done in Volhard's process, is necessary, two samples of iron were analyzed, first by solution in nitric acid followed by evaporation with sulphuric acid, and second by solution in nitric acid and direct precipitation. The results were:

I.

	Nitric and sulphuric acids.	Nitric acid.
	0.335	0.344
	0.348	0.326
	0.332	0.329
Mean,	0.338	0.333

II.

	0.392	0.404
	0.408	0.412
Mean,	0.400	0.408

It is evident that the evaporation with sulphuric acid is unnecessary and the saving effected here nearly or quite compensates for the extra precipitation as compared with Volhard's method.

As solution is more certain to be complete, for some irons, in a mixture of nitric and hydrochloric acids than in nitric acid alone, Mr. R. C. Warren has made some comparative determinations with these two solvents.

I.

	Nitric acid.	Nitric and hydrochloric acids.
	0.189	0.207
	0.196	0.213
	0.207	0.207
	0.210	....
Mean,	0.200	0.209

II.

	0.302	0.306
	0.310	0.302
Mean,	0.306	0.304

The precipitation of the manganese dioxide appears to take place a little more easily from the solution in which hydrochloric acid has been used.

The method resembles Volhard's method as described by Blair in his "Chemical Analysis of Iron," more closely than any other. It has the advantage of avoiding the evaporation with sulphuric acid to destroy carbonaceous matter required by that method. It also gives a sharp end reaction. Not only is the end in titrating a neutral manganese solution with permanganate difficult to hit, but it is very uncertain because of the catalytic action of manganese dioxide in causing the decomposition of potassium permanganate.[1]

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[1] Morse, Hopkins and Walker: *Am. Chem. J.*, **18**, 401.