

Nickel. Exner's conditions for nickel¹ served very well for the determination of this metal. There was no decided preference in the use of ammonium sulphate and ammonium hydroxide; or ammonium acetate and ammonium hydroxide as the electrolytes. The strong alkaline solutions should not stand longer than momentarily in the tin, unprotected by a current, but it is not necessary to have the circuit closed before putting in the reagents. The deposits were gray and very compact. A slight amount of loose material may be brushed out and the dish used for another determination, but if too thick a coating of nickel is deposited it will be found very difficult to remove. The nickel was dissolved with potassium cyanide aided by the current or by nitric acid, specific gravity 1.52.

TABLE XI

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ = Ni in grams	30 pct. aprotic acid in cc.	NH_4OH Sp. Gr. 0.99 in cc.	Volume in cc. when diluted	Approximate temp. at start	Current N.D.P. mA	Volts	Time in minutes	Ni deposited in gms.	Error in pct. of Ni in $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
0.2500	10	30	100	65°	5	9	13	0.2497	0.03
"	"	"	"	"	"	"	14	0.2502	0.02
"	"	"	"	"	"	"	13	0.2496	0.03
"	"	"	"	"	"	"	"	0.2500	0.00
"	"	"	"	"	"	"	"	0.2504	0.03
"	"	"	"	"	6	"	"	0.2491	0.08
"	"	"	"	"	6	"	"	0.2495	0.04
"	"	"	"	"	"	"	"	0.2501	0.01

Note: Speed of the rotator was about 700 R. P. M.

TABLE XII

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ = Ni in grams	$(\text{NH}_4)_2\text{SO}_4$ in grams	NH_4OH Sp. Gr. 0.99 in cc.	Volume in cc. when diluted	Approximate temp. at start	Current N.D.P. mA	Volts	Time in minutes	Ni deposited in grams	Error in pct. of Ni in $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
0.2500	1.5	25	100	65°	5	8-10	15	0.2500	0.00
"	"	"	"	"	"	"	"	0.2497	0.03
"	"	"	"	"	"	"	16	0.2504	0.03
"	"	"	"	"	"	"	15	0.2500	0.00

Note: This series was run by Mr. Hill. Speed of the rotator was about 550 R. P. M.

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THE DETERMINATION OF MANGANESE IN WATER.

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The need for a convenient method of determining manganese in water has been recognized by many analysts. In the ordinary practice of the water analyst either the determination is made gravimetrically or it is omitted.

Manganese together with iron occurs in many ground waters, and very often its presence complicates or vitiates the processes used for the re-

¹ This Journal, 25, 899.

removal of iron from water supplies. At Breslau, in 1904, the sudden presence of manganese in the ground water made the supply useless for a time, notwithstanding the fact that the water was treated by aeration and filtration for the purpose of removing the iron from it.

Extremely valuable data are missing because of the inconveniences of the present time-consuming methods for the determination of manganese. Such data will be collected only if the methods be as facile as other methods used in water analysis. Waters rarely contain more than 10 milligrams of manganese in a liter. Gravimetric methods are often beyond consideration, and the only ones which seem generally practicable are those in which the manganese is oxidized to permanganic acid. Of these latter the lead oxide methods of Chatard and others¹ and the sodium bismuthate method seemed to be the most promising. The sodium bismuthate method was used because of the greater ease with which the solution could be freed from the precipitate. This method has been used for the determination of manganese in ores and steels and is described by Blair². It was proposed by Schneider³ and modified first by Reddrop and Ramage⁴ and then by Bearley and Ibbotson.⁵

The method is based upon the fact that in the presence of an excess of nitric acid a manganous salt is oxidized to permanganic acid by bismuth tetroxide. Blair states that :—

"The permanganic acid formed is very stable in nitric acid of 1.135 sp. gr. when the solution is cold, but in hot solutions the excess of bismuth tetroxide is rapidly decomposed and then the nitric acid reacts with the permanganic acid and as soon as a small amount of manganous salt is formed the remainder of the permanganic acid is decomposed, manganous nitrate dissolves and manganese dioxide precipitates."

Reddrop and Ramage showed that it was difficult to get bismuth tetroxide free from chlorides, the presence of which would vitiate results, so they proposed the use of sodium bismuthate.

The manganese in the permanganic acid produced by oxidation may be determined in two ways. After filtering off the excess of bismuthate Blair adds an excess of ferrous sulphate to the filtrate and by titration with permanganate solution determines the amount necessary to deoxidize the permanganic acid. For waters containing less than 1 milligram of manganese, however, comparison of the filtrate colorimetrically with permanganate run from a burette into an equal volume of dilute sulphuric acid free from organic matter contained in a Nessler tube, proved to be simpler and more precise; for larger quantities, however, the titration method should be used.

¹ Sutton's Volumetric Analysis.

² This Journal, 26, 793.

³ Dingler, pol. J., 269, 224.

⁴ J. Chem. Soc., 1895, 268.

⁵ The Analysis of Steel Works Materials.

Method.

Evaporate with about 25 cc. of nitric acid (sp. gr. 1.135) enough of the sample of water to give from 0.01 to 1 mg. of manganese. Gently ignite the residue or bake it for $\frac{1}{2}$ hour at 130°. Add 50 cc. of nitric acid (sp. gr. 1.135) and when the solution is cool add about 0.5 gram of sodium bismuthate. Heat until the pink color disappears.

At this point Blair, in his determination of manganese in iron, adds sulphurous acid, ferrous sulphate or sodium thiosulphate, to clear the solution if manganese dioxide is precipitated, and heats it to dispel all oxides of nitrogen. With waters this step was usually unnecessary, but whenever so, thiosulphate was the reagent used.

To the cool solution add sodium bismuthate in excess, stir a few minutes, and filter through thoroughly washed asbestos in a Gooch filter. Wash with dilute nitric acid, transfer filtrate to a large Nessler tube, and make up to 100 cc. with dilute nitric acid.

In another tube put 100 cc. of dilute sulphuric acid and add standard potassium permanganate solution until the color of the sample is matched. The volume of potassium permanganate in cc. \times 0.0001 gives the weight of manganese in grams. Express results as parts per million, — milligrams per liter.

Reagents.

Potassium Permanganate Solution.—Dissolve 0.288 gram of potassium permanganate in water and make up to 1 liter. 1 cc. is equivalent to 0.1 mg. manganese.

Nitric Acid (sp. gr. 1.135). A mixture of 3 parts of water and 1 part of strong nitric acid (sp. gr. 1.42) is used.

Dilute Nitric Acid. 30 cc. of strong nitric acid to the liter.

Sulphuric Acid. 25 cc. of pure concentrated sulphuric acid to the liter. Add enough permanganate to color the solution slightly but perceptibly pink.

Asbestos. Prepare asbestos in the usual way by washing with acid and igniting. It should be free from organic matter.

Notes and Precautions.

The first experiments with this method gave unsatisfactory, erroneous results. Each reagent was tested to ascertain the cause of the error. It was found that the "C.P." nitric acid used was impure; it contained oxides of nitrogen. Several methods of purification were tried. The most efficient process proved to be that of passing a current of air through the concentrated acid for about half an hour.

The presence of organic matter also vitiates results; when in large amounts the color of permanganic acid does not appear in the filtrate. This difficulty is overcome by ignition of the residue or by baking it for

$\frac{1}{2}$ hour at 130° . The asbestos must be free from organic matter; otherwise the permanganic acid will be reduced.

The presence of chlorides also interferes with the determination. Samples which contain large amounts of chlorine should be treated before evaporation with a slight excess of silver nitrate and then filtered.

Experiments were made in which the bismuthate was added but once, the excess filtered off immediately, and the permanganic acid determined. Satisfactory results, however, were not obtained by this shorter method. The oxidation is complete only after the second addition of bismuthate.

The method is very delicate. It will detect 0.0002 gram of manganese.

Experiments.

The first experiments were made with distilled water and known solutions of manganese sulphate and potassium permanganate. The results were as follows:—

A. WITH MANGANESE SULPHATE		
No.	Grams Manganese Added	Grams Manganese Recovered
1	0.00010	0.00009
2	0.00010	0.00010
3	0.00010	0.00010
4	0.00050	0.00050

B. WITH POTASSIUM PERMANGANATE		
No.	Grams Manganese Added	Grams Manganese Recovered
1	0.00010	0.000095
2	0.00020	0.00020
3	0.00050	0.00045

C. *Effect of Organic Matter.*—Experiments were made like the above, except with the addition of varying volumes of leaf infusion, this being considered typical of the organic matter contained in water. The results were as follows:—

(a) WITHOUT IGNITION OF RESIDUE			
No.	Grams of Manganese Added	cc. Leaf Infusion	Grams of Manganese Recovered
1	0.00010	1	0.00010
2	0.00010	2	0.00008
3	0.00010	10	0.00007
4	0.00010	25	Color faded in 5 min.

(b) RESIDUE IGNITED			
No.	Grams of Manganese Added	cc. Leaf Infusion	Grams of Manganese Recovered
1	0.00010	25	0.00010
2	0.00010	25	0.00010

D. Two trials of the method were made, first with Boston water, a surface supply, and second with Reading water, a ground water supply containing about 2 parts per million of iron. The Boston water contains no appreciable amount of manganese, but manganese is present in the

Reading water. Besides determining the manganese in the water, determinations were made with the water containing varying amounts of added manganese.

(a) BOSTON WATER

No.	cc. taken	Grams of Manganese Added	Grams of Manganese Recovered
1	100	0.00000	0.00000
2	100	0.00010	0.00009
3	100	0.00010	0.00010
4	100	0.00010	0.00009

(b) READING WATER

No.	cc. taken	Grams of Manganese Added	Grams of Manganese Recovered
1	100	0.00000	0.000065
2	100	0.00000	0.000070
3	100	0.00000	0.000075
4	100	0.00010	0.000170
5	100	0.00010	0.000170
6	100	0.00010	0.000165

E. The following experiment shows the effect upon the determination of large amounts of chlorine.

No.	cc. Boston City Water	mg. Chlorine added to a liter	Grams Manganese Added	Grams Manganese Recovered
1	1000	50	0.00010	0.000085
2	1000	500	0.00010	0.000075
3	100	50	0.00010	0.000079
4	100	500	0.00010	0.000080
5	100 ¹	500	0.00010	0.000080

The writer finds this method rapid, convenient, serviceable, and reasonably accurate. He recommends it to other analysts with the hope that more data regarding the manganese content of ground waters may be placed on record.

He also wishes to thank his friend, Professor Henry Fay, for fundamental suggestions, and to acknowledge the services of his assistant, Miss Grace Ide Fairchild, who has made most of the determinations.

14 BEACON ST., BOSTON, April 15, 1907.

A RAPID METHOD FOR THE DETERMINATION OF CALCIUM IN WATER, AND ITS SIGNIFICANCE IN CONNECTION WITH THE ANALYSIS OF WATER FOR BOILER PURPOSES.

BY F. E. HALE.

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In the examination of water for boiler purposes it is extremely important to be able to determine the relative amounts of calcium and magnesium salts present. The determination of the total hardness by the

¹ Boston water contains about 2.5 parts of chlorine per million.