

RESULTS ON MONAZITE SANDS (*continued*).

	Meta-nitrobenzoic.	Modified metanitrobenzoic.	Fumaric.	Combination.
North Carolina monazite	5.48	5.27	5.13	5.39
	5.12	5.26	...	...
	...	5.27	...	...
Brazil monazite	4.89	4.99	4.85	4.90
	4.97	4.98	...	...
	5.04	4.82	...	...
High-grade North Carolina monazite <sup>1</sup>	6.04	6.02	5.89	5.98
	6.15	6.04	...	...
	5.88	5.88	...	...
Refined Brazil monazite <sup>1</sup>	...	6.15	...	...
	...	5.81	5.71	5.97
	...	5.71	...	...

## CONCLUSIONS.

(1) Metanitrobenzoic acid precipitates thorium quantitatively as  $\text{Th}(\text{C}_6\text{H}_4\text{NO}_2\text{CO}_2)_4$  from a neutral solution of the nitrate.

(2) When this precipitation is repeated, it affords a complete separation from cerium, lanthanum and didymium.

(3) This method gives as good results for thorium in monazite as the combination or fumaric acid methods, and has the advantage in that it is much shorter, and offers no difficulties in precipitation or filtration; the precipitant is not expensive and avoids the use of alcohol.

This investigation was carried out under the direction of Professor Edmund H. Miller, and I wish to gratefully acknowledge my indebtedness to him for his kind interest and advice.

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## THE BISMUTHATE METHOD FOR THE DETERMINATION OF MANGANESE.

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THIS method was originally proposed by Schneider,<sup>3</sup> and modified first by Reddrop and Ramage,<sup>4</sup> and then by Brearley and Ibbotson.<sup>5</sup>

<sup>1</sup> From the original sample received from Professor Baskerville, not the same as used by Metzger. This Journal, 24, 901 (1902).

<sup>2</sup> The digestion for these lasted three hours.

<sup>3</sup> Ding. poly. J., 269, 224.

<sup>4</sup> Trans. Chem. Soc., 1895, p. 268.

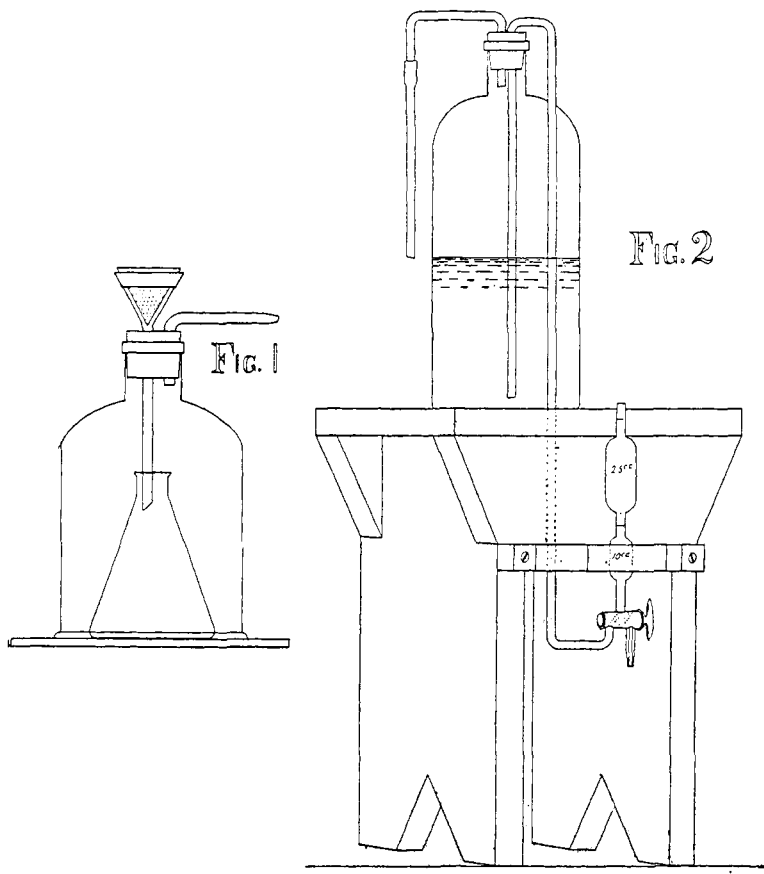
<sup>5</sup> "The Analysis of Steel Works Materials."

The method was based on the fact that a manganous salt in the presence of an excess of nitric acid is oxidized to permanganic acid by bismuth tetroxide. 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 the 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.

In the cold, however, the excess of the bismuth salt may be filtered off and to the clear filtrate an excess of ferrous sulphate added and the amount necessary to deoxidize the permanganic acid determined by titrating with permanganate. The end reactions are very sharp and the method is extremely accurate, but the presence of even traces of hydrochloric acid utterly vitiate the results. As pointed out by Reddrop and Ramage, bismuth tetroxide which was used by Schneider is difficult to obtain free from chlorides and they recommended sodium bismuthate, which they prepare as follows: Heat 20 parts of caustic soda nearly to redness in an iron or nickel crucible and add, in small quantities at a time, 10 parts of basic bismuth nitrate, previously dried in a water-oven. Then add 2 parts of sodium peroxide and pour the brownish yellow fused mass on an iron plate to cool; when cold, break it up in a mortar, extract with water and collect on an asbestos filter. The residue, after being washed four or five times by decantation, is dried in the water-oven, then broken up and passed through a fine sieve. (The Baker & Adamson Chemical Co. have prepared sodium bismuthate in this manner which is perfectly free from manganese chlorides and has proved entirely satisfactory.)

#### THE METHOD.

*Steels.*—Dissolve 1 gram of drillings in 50 cc. of nitric acid (sp. gr. 1.135) in an Erlenmeyer flask of 200 cc. capacity. Cool and add about 0.5 gram of bismuthate. The bismuthate may be measured in a small spoon and experience will soon enable the operator to judge of the amount with sufficient accuracy. Heat for a few minutes, or until the pink color has disappeared, with or without the precipitation of manganese dioxide. Add sulphurous acid, solution of ferrous sulphate or



sodium thiosulphate in sufficient amount to clear the solution and heat until all nitrous oxide has been driven off. Cool to about  $15^{\circ}$  C., add an excess of bismuthate and agitate for a few minutes. Add 50 cc. of water containing 30 cc. of nitric acid to the liter and filter through an asbestos felt on a platinum cone into a 300 cc. Erlenmeyer flask and wash with 50 to 100 cc. of the same acid. The arrangement shown in Fig. 1 has proved very satisfactory. Run into the flask from the pipette, shown in Fig. 2, a measured volume of ferrous sulphate solution and titrate to a faint pink color with permanganate. The number of cubic centimeters of the permanganate solution obtained, subtracted from the number corresponding to the volume of ferrous

sulphate used, will give the volume of permanganate equivalent to the manganese in the sample, which, multiplied by the value of the permanganate in manganese, gives the amount of manganese in the steel.

*Pig Iron.*—Dissolve 1 gram in 25 cc. of nitric acid (sp. gr. 1.135) in a small beaker and as soon as the action has ceased filter on a 7 cm. filter into a 200 cc. Erlenmeyer flask, wash with 30 cc. of the same acid and proceed as in the case of steels.

In the analysis of white irons it may be necessary to treat the solution several times with bismuthate to destroy the combined carbon. The solution, when cold, should be nearly colorless; if not, another treatment with bismuthate is necessary.

*Iron Ores Containing Less than 2 Per Cent. of Manganese.*—Treat 1 gram in a platinum dish or crucible with 4 cc. of strong sulphuric acid, 10 cc. of water and 10 to 20 cc. of hydrofluoric acid. Evaporate until the sulphuric acid fumes freely. Cool and dissolve in 25 cc. of 1.135 nitric acid. If no appreciable residue remains, transfer to a 200 cc. Erlenmeyer flask, using 25 cc. of 1.135 nitric acid to rinse the dish or crucible and proceed as usual. If there is an appreciable residue, filter on a small filter into a beaker, wash with water, burn the filter and residue in a crucible and fuse with a small amount of potassium bisulphate. Dissolve in water with the addition of a little nitric acid, add to the main filtrate, evaporate nearly to dryness, take up in 1.135 nitric acid and transfer to the flask as before.

*Manganese Ores and Iron Ores High in Manganese.*—Treat 1 gram as in the case of iron ores, using a little sulphurous acid, if necessary. Transfer the solution to a 500 cc. flask, dilute to the mark, mix thoroughly and measure into a flask from a carefully calibrated pipette such a volume of the solution as will give from 1 to 2 per cent. of manganese and enough strong nitric acid (sp. gr. 1.4) to yield a mixture of 1.135 acid in a volume of 50 to 60 cc. For example, in a 50 per cent. ore use 10 cc. of the solution and add 30 cc. of water and 10 cc. nitric acid (sp. gr. 1.4). In this case the manganese must be calculated on  $\frac{1}{50}$  of a gram or 20 mg. of ore. When working on such amounts it is always desirable to make duplicate analyses and take the mean, as a difference of 0.1 cc. makes a large error in the result. When the ore contains a much smaller amount of manganese,

say 5 or 10 per cent., it is better to make up the solution to say 100 cc. instead of 500.

*Ferro-manganese.*—Treat 1 gram exactly like steel. Dilute to 500 or 1000 cc. and proceed as in manganese ores.

*Ferro-silicon.*—Treat 1 gram with sulphuric and hydrofluoric acids and proceed as with iron ores.

*Special Steels.*—Steels containing chromium offer no special difficulties except that it must be noted that while in hot solutions the chromium is oxidized to chromic acid, which is reduced by the addition of sulphurous acid, the oxidation proceeds so slowly in cold solutions that if there is no delay in the filtration and titration the results are not affected. Steels containing tungsten are sometimes troublesome on account of the necessity for getting rid of the tungstic acid. Those that decompose readily in nitric acid may be filtered and the filtrate treated like pig iron, but when it is necessary to use hydrochloric acid it is best to treat with *aqua regia*, evaporate to dryness, redissolve in hydrochloric acid, add a few drops of nitric acid, dilute, boil and filter. Get rid of every trace of hydrochloric acid by repeated evaporations with nitric acid and proceed as with an ordinary steel.

#### REAGENTS.

*Nitric Acid (sp. gr. 1.135).*—A mixture of 3 parts of water and 1 part strong nitric acid answers perfectly for this purpose.

*Nitric Acid (3 per cent.)*—Thirty cc. of strong nitric acid to the liter.

*Permanganate Solution and Ferrous Sulphate Solution.*—One gram of potassium permanganate to the liter gives a solution of convenient strength, and 12.4 grams of ferrous ammonium sulphate and 50 cc. of strong sulphuric acid,<sup>1</sup> made up to 1 liter, gives a solution which is almost exactly equal to the permanganate solution. As the strength of the ferrous sulphate solution changes quite rapidly, while the permanganate remains unaltered for months, it is unnecessary and troublesome to attempt to keep them of the same strength. By using a constant volume of the ferrous sulphate solution and testing it against the permanganate solution every day the calculation of the results is very simple. It is necessary that the conditions should be the

<sup>1</sup> Dr. C. B. Dudley proposes to use 25 cc. of sulphuric and 25 cc. of strong phosphoric acid as tending to give a more nearly colorless solution.

same in getting the strength of the ferrous sulphate solution as in titrating a solution for manganese, and after many experiments the following method of procedure was adopted: Measure into a 200 cc. flask 50 cc. of nitric acid (sp. gr. 1.135), cool and add a very small amount of bismuthate, dilute with 50 cc. of 3 per cent. nitric acid, filter into a 300 cc. flask and wash with 50 cc. of 3 per cent. nitric acid. If the felt is well coated with bismuthate it is unnecessary to add any to the nitric acid in the flask, as filtration through the mass of bismuthate on the felt will answer the purpose. Run in from the pipette (Fig. 2) 25 cc. of ferrous sulphate solution and titrate with the permanganate to a faint pink. This gives the value in permanganate of the ferrous sulphate solution. With this method of procedure the discrepancies that had occurred entirely disappeared and it is possible to make any number of determinations with a variation of less than 0.1 cc.

The permanganate solution may be standardized in three ways:

First, by getting its value in iron in the usual way and calculating its value in manganese. The proportion is 56:55, or as 1:0.98214.<sup>1</sup>

Second, by titrating a steel with a known amount of manganese and getting the value of the solution by dividing the percentage of manganese by the number of cubic centimeters of the permanganate used.

Third, by making a solution of pure manganese sulphate and determining the manganese in it by evaporating a weighed amount of the solution to dryness, heating to dull redness and weighing as manganese sulphate, which, multiplied by 0.36424, gives the amount of manganese. Five grams of "C. P." manganese sulphate dissolved in 500 cc. of water and filtered will give a solution containing about 0.0035 gram of manganese to the gram of solution. Weigh 1 to 3 grams of the solution in a crucible, transfer to a 200 cc. flask, using 50 cc. of nitric acid (sp. gr. 1.135), cool, add 0.5 to 1 gram bismuthate and allow it to stand for three or four minutes, shaking at intervals. Add 50 cc. of 3 per cent. nitric acid and filter through the asbestos filter and wash with 50 or 60 cc. of the same acid. Run 25 cc. of the ferrous sulphate solution into the flask from the pipette and titrate with the permanganate solution to a faint pink. Subtract the

<sup>1</sup> With the atomic weights now accepted this would be 55.9:55 = 0.9839.—EDITOR.

number of cubic centimeters of the permanganate solution obtained from the value of the 25 cc. of ferrous sulphate solution in permanganate and the result is the number of cubic centimeters of the permanganate corresponding to the manganese in the manganese sulphate solution used. Divide the weight of the manganese in the manganese sulphate used by the number of cubic centimeters of permanganate and the result is the value of 0.006354 gram, or the sample contains 0.635 per cent. manganese.

*Example.*—One gram manganese sulphate solution contains 0.003562 gram manganese; 2.0372 grams manganese sulphate solution equals 0.0072565 gram manganese; 25 cc. ferrous sulphate solution equals 24.5 cc. permanganate solution; 2.0372 grams manganese sulphate, after oxidation and addition of 25 cc. ferrous sulphate solution, require 3.6 cc. permanganate solution; 24.5 cc. — 3.6 cc. = 20.9 cc.; 0.0072565 divided by 20.9 = 0.0003472, or 1 gram permanganate equals 0.0003472 gram manganese. If then 1 gram of steel, after oxidation and addition of 25 cc. ferrous sulphate solution, requires 6.2 cc. permanganate solution to give the pink color,  $24.5 - 6.2 = 18.3 \times 0.0003472 = 0.006354$  gram, or the sample contains 0.635 per cent. manganese.

#### NOTES AND PRECAUTIONS.

The delicacy of the reaction of manganese in nitric acid solution with sodium bismuthate is extraordinary. 0.000005 gram of manganese gave an appreciable color in 50 cc. of solution.

When the proper precautions are observed, this method for materials containing small amounts of manganese, say up to 2 per cent., is more accurate than any other method, volumetric or gravimetric, that I have ever used.

As will be seen in the description of the various methods of solution, the use of hydrochloric acid has been avoided because the presence of even traces of this reagent is fatal to the accuracy of the method. Where it is impossible to avoid its use and its presence is suspected in the final nitric acid solution, the addition of a drop or two of silver nitrate will overcome the difficulty, but the filter must be rejected after using it for filtering a solution so treated.

Any form of asbestos filtering tube may be used for filtering off the bismuthate, but the perforated cone with bell jar, shown in Fig. 1, is the most satisfactory, because it has the largest area

of filtering surface. One filter may be used for fifty or more determinations and the time occupied in filtering and washing one determination is only from one minute and a half to three minutes. The filtrate must be perfectly clear, for the least particle of bismuthate carried through will vitiate the result by reacting with the excess of ferrous sulphate. As soon as the filtration and washing are completed, the ferrous sulphate should be added and the excess titrated with the permanganate solution, as the permanganic acid gradually decomposes on standing and the warmer the solution the more rapid is the decomposition. At a temperature of  $5^{\circ}$  C. the solution will remain unaltered for several hours, but at  $40^{\circ}$  C. fifteen minutes will show an appreciable change. The larger the amount of manganese the more rapid the change. It is especially important not to allow the solution to stand after adding the ferrous sulphate, as the excess of this reagent reacts with the nitric acid in a few minutes and the formation of the smallest amount of nitrous oxide is fatal to the accuracy of the determination. For this reason it is important to boil off every trace of nitrous oxide when in the earlier part of the operation sulphurous acid or other deoxidizing agent is added.

When working with steels of unknown manganese content, it may often happen that 25 cc. of ferrous sulphate solution are insufficient to entirely reduce the permanganic acid, in which case an additional amount of ferrous sulphate must be added and the pipette shown in Fig. 2 has been arranged to meet this contingency. It will be noticed that the solution of permanganic acid upon the addition of an insufficient amount of ferrous sulphate does not necessarily retain its pink or purple color, but usually changes to a dirty brown. When this occurs, the lower part of the pipette may be emptied directly into the flask and the value of the two parts taken as the amount from which the number of cubic centimeters of permanganate corresponding to the excess of ferrous sulphate must be subtracted. When the sample is low in manganese, the 10 cc. portion of the pipette alone may be used, so that the arrangement allows a great deal of variation in the manganese content of the samples worked on.

There is no advantage in using permanganate solutions differing in strength from the one given above, but the strength of



the ferrous sulphate solution may be changed to meet special cases.

I am surprised that this method has not come into general use, for it combines in a remarkable degree extreme accuracy and great rapidity with simplicity and ease of manipulation.

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## THE DETERMINATION OF SULPHUR IN IRON.

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A PAPER on this subject by the same authors was read before the American Chemical Society at its meeting in Cleveland in June, 1903, in which paper the authors took a somewhat different view of the subject, in part at least, from that ordinarily taken, and expressed the opinion that this or that method was not responsible for all the trouble experienced in getting close checks on sulphur determinations, but that much of the trouble was due to the analyst through carelessness, inability or inexperience.

In the present article the substance of that paper will be used, rewritten in part, together with some additions based on the results of further experiments.

We wish to emphasize the fact as pointed out in the paper mentioned that the determination of sulphur in iron is as difficult probably as any the iron chemist is called upon to make, and the young man of limited experience who may perchance have trouble with it must by no means feel that his career as a chemist is ended, and we also wish to say that we believe there is much to be said in regard to the relative merits of different methods—which phase of the question will be considered later—but at the same time we firmly believe that a competent chemist should be willing to sign his reports with his name instead of the method he used. We would not decry the principle of standard methods, as in the main they are excellent, but a too rigid application of that principle tends to relieve the analyst of responsibility—this too when the personal element cuts so large a figure that two operators using the same method described in minutest detail (and this is particularly true