[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

THE INTERFERENCE OF COBALT IN THE BISMUTHATE METHOD FOR MANGANESE[1]

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The conditions recommended by Blum[3] for the determination of manganese by the bismuthate method are as follows: "To the manganese solution containing 20 to 40% (by volume) of nitric acid (free from nitrous acid) in a volume of 50 to 150 cc., add a slight excess of bismuthate (usually 0.5 to 1.0 g.), agitate thoroughly for about one-half minute, wash down the sides of the flask with 3% nitric acid, filter through asbestos, wash with 100 cc. of 3% nitric acid, add a slight excess of ferrous sulfate, and titrate at once with permanganate."

To these may be added the following: (1) the solution should not contain more than 0.05 g. of manganese; (2) moderate amounts of sulfuric acid are not harmful, as for instance 5 cc. of sulfuric acid and 10 cc. of nitric acid in a 50 cc. solution; (3) chlorides must be absent; (4) the temperature of the solution may be varied from 5° to 25°; (5) one-half minute is enough for the reaction if the solution is agitated, but a longer period will do no harm; (6) new, and also stored, bismuthate should be tested for its oxidizing power; this is easily done by trying the bismuthate method on portions of permanganate solution which have been reduced and comparing the consumption of ferrous sulfate with that obtained by direct titration; (7) unless the asbestos has been *very carefully* freed from hydrochloric acid and chlorides, the first run through it will always be low; to make certain, it is well to pass through the filter a dil. nitric acid solution of permanganate containing a small amount of bismuthate and then to wash it with 3% nitric acid before regular filtration; (8) the ferrous sulfate solution should not be allowed to stand for more than 10 minutes before the titration with permanganate, and its permanganate equivalent is best found by the titration of a suitable volume of ferrous sulfate which has been added to the filtrate obtained in a blank run on the bismuthate, acid, filtration, etc.; (9) the permanganate solution which may be either 0.03 or 0.1 N depending on the percentage of manganese involved is best standardized against sodium oxalate as described by McBride,[4] and a properly prepared and filtered solution should preserve its strength for several

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[3] Reprint 186 of the *Bulletin* of the Bureau of Standards, **8**, 736 (1912). THIS JOURNAL, **34**, 1395 (1912).

[4] McBride, *ibid.*, **34**, 415 (1912).

months exposed to diffused light, if protected from dust and reducing substances. In the presence of the latter, solutions containing potassium hydroxide decompose less rapidly than do neutral solutions.[3]

For amounts of manganese up to 0.05 g. the accuracy of the above method can be safely regarded as within 1 part in 500. The procedure is singularly free from interference by other elements, and the only elements that have been recognized as troublesome are chromium and cerium. Some elements introduce minor difficulties as, for example, the color interference of concentrated solutions of copper or nickel salts, the delayed end-point caused by vanadium, the slightly low results caused by antimony, and the slightly high results caused by silver.

Vanadium causes trouble because it is at first oxidized to the quinquevalent state, then reduced to the quadrivalent condition, and finally reoxidized with some difficulty by the very small excess of permanganate which is permissible at the end-point. If it is not completely reoxidized, the results for manganese will of course be high.

Antimony is also oxidized to the quinquevalent state by sodium bismuthate, but only a very small part is reduced by ferrous sulfate in the cool solution which is employed. In further contrast to vanadium, antimony causes the results to be slightly low as, for example, 0.0109 instead of 0.0111 g. of manganese in the presence of 0.05 g. of antimony. Neither the cause of the error nor any remedy save prior removal of the antimony or the use of another method is known to me. If another method is used, Ford's[5] is to be preferred for accurate analyses, and the persulfate-arsenite method for routine analyses.

Silver introduces slight difficulties as it causes the formation of oxides of nitrogen. The effect is not serious with ordinary amounts of silver as shown by the results 0.0112 and 0.0113 instead of 0.0111 g. of manganese in the presence of 0.01 and 0.1 g., respectively, of silver.

Chromium interferes because it is never completely oxidized at any stage. Only a part of it is oxidized by bismuthate and permanganic acid at the start; this is then reduced by ferrous sulfate, and finally a much smaller part is reoxidized during the final titration. Chromium therefore tends to cause results for manganese to be high. As either oxidation proceeds slowly in cool solutions, good results for manganese can be obtained in the routine analysis of steels containing moderate amounts of chromium and no vanadium by working rapidly ($^1/_2$ to 1 minute reaction) with solutions at a temperature not over 20°. Under such conditions, and especially if ice-cold solutions are used, vanadium causes some trouble as it is reoxidized with difficulty. Hence, such a method works quite well with chrome-nickel, but not so well with chrome-vanadium steels.

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[5] Blair, "The Chemical Analysis of Iron," 8th ed., J. B. Lippincott and Co., **1918**, pp. 108–110.

Satisfactory results can be achieved with both steels by using suitable reducing solutions in place of ferrous sulfate, as for example sodium arsenite or mercurous nitrate, which reduce permanganate but not chromate or vanadate.

Cerium is rapidly oxidized to the quadrivalent state by bismuthate (even in cold solution) and subsequently reduced by ferrous sulfate to the trivalent state.[6] Hence cerium will cause high results for manganese unless it is previously removed or a proper reducing agent, such as sodium arsenite, substituted for ferrous sulfate.

Cobalt, in contrast with all of the above, is a real interfering element in the bismuthate method and must be removed if bismuthate is to be used.[7] This follows because it is oxidized by bismuthate at all temperatures that are permissible for manganese, and the oxidized compound reacts with both ferrous sulfate and permanganic acid. Cobalt upon oxidation approaches the formula Co_3O_4 and the color changes from pink to green.[8] The oxidized compound reacts with ferrous sulfate, but not directly with permanganic acid. If, however, it is first treated with manganous nitrate and then with permanganate, a reaction does take place as evidenced by a change of color to an amber tint. This solution in the course of time shows a reappearance of the permanganate tint and yields a brown deposit of manganese dioxide together with some oxide of bismuth. The reaction between the oxidized cobalt compound and permanganic acid waits, therefore, upon some decomposition of the latter. When once started, it proceeds with considerable rapidity, and as the resultant compound does not react rapidly with ferrous sulfate, the net result is a lowered consumption of ferrous sulfate with consequent *low* values for manganese. The extent of the effect is indicated in Table I. In every case measured portions of a standard permanganate solution were reduced by sulfur dioxide, boiled to expel gas, cobalt was added as shown and then enough nitric acid to obtain 40 cc. of a 30% (by volume) solution. This solution was then cooled to 15–20°, treated with an excess of bismuthate, shaken occasionally during three minutes and then diluted with 50 cc. of 3% (by volume) nitric acid, filtered through asbestos and washed with the same acid. The solution was finally treated with a measured excess of ferrous sulfate and titrated with standard permanganate.

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[6] F. J. Metzger, This Journal, **31**, 523 (1909).

[7] So far as I know, no reference to its behavior in the bismuthate method has been made, save the note "This method (the bismuthate) cannot be used in the presence of cobalt" recommended by me and inserted in the Tentative Methods for the Analysis of Plain Carbon Steel, *Proc. Am. Soc. Testing Materials,* **22,** Part I, p. 589 (1922).

[8] A similar and striking change also takes place when a dil. sulfuric acid solution of cobalt sulfate is electrolyzed in a U-tube with moderately long limbs. The liquid in the cathode limb remains pink while that in the anode gradually turns green. Low current must be used, as the oxidized compound is unstable in a warm solution.

TABLE I

THE EFFECT OF COBALT IN THE BISMUTHATE METHOD FOR MANGANESE

Weight of manganese added, 0.0110 g.

Co added, g	none	none	0.001	0.005	0.010	0.020
Mn indicated, g	0.0110	0.0110	0.0107	0.0103	0.0101	0.0094
Error, mg	0.0	0.0	−0.3	−0.7	−0.9	−1.6

Somewhat better, though still unacceptable, results are obtained as shown in Table II, when the oxidized solution is titrated with sodium arsenite.

TABLE II

THE EFFECT OF COBALT IN THE BISMUTHATE-ARSENITE METHOD FOR MANGANESE

Weight of manganese added, 0.0110 g.

Co added, g	none	none	0.001	0.005	0.010	0.020
Mn indicated, g	0.0110	0.0110	0.0107	0.0106	0.0102	0.0102
Error, mg	0.0	0.0	−0.3	−0.4	−0.8	−0.8

It may be mentioned in passing that cobalt is not oxidized by persulfate in the hot acid solution which is employed for the oxidation of manganese and that, therefore, good results can be obtained in its presence through the use of the persulfate-arsenite method. For standardization work Ford's method[9] is to be preferred.

In conclusion, I hope that some reader may be stimulated to investigate various methods for the oxidation of cobalt in acid solution. If the oxidation can be carried to a definite stage we shall, of course, have an excellent method for the volumetric determination of cobalt in the presence of such elements as iron and nickel.

Summary

The proper conditions for the determination of manganese by the bismuthate method are reviewed and the interference of certain elements, notably cobalt, is discussed.

Cobalt is oxidized by bismuthate and the oxidized compound reacts with both ferrous sulfate and permanganate. The latter reaction does not start until some permanganate has been decomposed and then proceeds so rapidly that it causes low results for manganese.

In the presence of cobalt, Ford's method is to be preferred for accurate analyses and the persulfate-arsenite method for routine work.

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[9] Ref. 5, pp. 108 and 110.