and others made on material subjected to the most approved methods of purification indicates that the material with which we worked was pure; but even with the large quantities which we had, we were unable to find any indication of a progressive diminution of the atomic weight of tellurium.

UNIVERSITY OF CALIFORNIA, May, 1912.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, COLLEGE OF THE CITY OF NEW YORK.]

A STUDY OF THE SENSITIVENESS OF THE BEAD AND LEAD DIOXIDE TESTS FOR MANGANESE WITH SPECIAL REFERENCE TO THE INTERFERENCE OF IRON.[1]

BY L. J. CURTMAN AND A. D. ST. JOHN.

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The object of this work was to determin, first, the delicacy of the bead and lead dioxide tests for manganese when this metal alone is present and, second, the influence of iron on these tests, since in the ordinary qualitative procedure, the manganese and iron are tested for in the same precipitate.

The Bead Test.—The bead tests were made in the customary way; that is, a sodium carbonate bead on a loop of platinum wire of approximately 3 mm. in diameter with a volume of about 0.03 cc. was fused with a small quantity of the metallic compound, slightly cooled, and then touched while still quite hot to powdered potassium chlorate. A special procedure, referred to below as "reheating," consisted in bringing the carbonate bead containing the manganese compound and adhering potassium chlorate into the upper part of the Bunsen flame, heating to quiet fusion,[2] and finally cooling, preferably by contact with a cold surface, such as a porcelain plate, until almost cold. By this "reheating" process a more intense coloration was produced, and in cases where large amounts of iron were present, it had the effect of concentrating the coloration in certain parts of the bead notably near the wire.

Tests were first made to determin the minimum quantity of manganese which would give a green coloration to the bead. To this end, one drop (0.05 cc.) of a standard manganese chloride solution was carefully absorbed in a sodium carbonate bead that had been previously fused and cooled; the wet mass was then slowly and cautiously dried by heating the wire (away from the bead) and finally fused and brought in contact with potassium chlorate. This procedure obviated the apparent difficulty of in-

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[1] Read before Section I (Analytical Chemistry) of the Eighth International Congress of Applied Chemistry, September 11, 1912.

[2] Care must be exercised in this fusion to lose none of the bead through sputtering, which may be caused by the use of too much chlorate or by too rapid heating.

troducing quantitative amounts of precipitate into the bead and was the method employed in all the bead tests except where otherwise stated. The following results were obtained:

TABLE I.

Substance $MnCl_2.4H_2O$.

Quantity of Mn.	Result.
0.05 mg.	Very good green
0.02 mg.	Very good green
0.005 mg.	Good green
0.002 mg.	Fair green
0.001 mg.	Doubtful but fair on reheating
0.0005 mg.	Trace of green on reheating—limit

If we consider the volume of the bead 0.03 cc. and its sp. gr. 1 (in order to make a rough comparison with other color reactions which are carried out in aqueous solution), the limiting test would show a delicacy of one part in 60,000.

Having determined the sensitiveness of the test when manganese alone is present, the next step was to investigate the interfering influence of iron. Accordingly, standard solutions of $FeCl_3.6H_2O$ and $MnCl_2.4H_2O$ were mixed in varying proportions and precipitated by the addition of an excess of sodium hydroxide. A small portion of the filtered precipitate was taken up on the bead and the test completed in the usual way. The following results were obtained:

TABLE II.

Parts Mn.	Parts Fe.	Result.
1	1	Very good
1	2	Very good
1	3	Good
1	4	Fair
1	5	Fair
1	6	Fair

Up to this ratio a small amount of the wet precipitate was used equal to about one-quarter of the bulk of the bead. With increasingly large amounts of iron, however, more of the precipitate was taken up, and reheating resorted to with the following results:

TABLE III.

Parts Mn.	Parts Fe.	Result.
1	25	Good
1	50	Good
1	100	Good
1	500	Good
1	1000	Fair

In the last two tests the blast lamp was used, and a quantity of the precipitate equal approximately to three or four times the volume of the bead was taken up in small portions, successively dried, and reheated several times. These results suggested that the iron did not interfere except in so far as it prevented sufficient manganese from being introduced into the bead to give the test; for if the same quantity of precipitate is to be employed in each test, it is obvious that the higher the ratio of iron to manganese, the smaller will be the quantity of the latter that will be contained in the portion taken for the test. The tests were, therefore, repeated with sufficient manganese (0.005 mg.) in each case to give a good color and to this amount were added varying quantities of iron. In these tests the solutions were not precipitated but absorbed in the bead in the manner already described.

The following results were obtained:

TABLE IV.

Parts Mn.	Parts Fe.	Result.
1 (0.005 mg.)	100	Good
1 (0.005 mg.)	200	Good
1 (0.005 mg.)	500	Good
1 (0.005 mg.)	1000	Good
1 (0.005 mg.)	2000	Good

In all the above experiments the beads were reheated; in the last test, this was repeated several times, potassium chlorate being added at each reheating. The iron present in the above tests was vastly more than could be dissolved in the bead and, in consequence, appeared as a brown coating completely enveloping the bead and masking the green color due to the manganese; it was found, however, that by reheating several times with more potassium chlorate this coating was driven to one side, causing the green color beneath to be exposed. It, therefore, appears that provided enough manganese is introduced into the bead to give a fair test, the amount of iron present has no effect other than to enclose the bead in a brown coating, which difficulty may be overcome as indicated above.

The Lead Dioxide Test.—To determin the sensitiveness of this test when manganese alone is present, diminishing amounts of a standard solution of manganese chloride were treated in test tubes with one to two grams of lead dioxide,[1] 0.5 cc. concentrated nitric acid and sufficient water to make the total volume 5 cc. The mixture was then gently boiled, allowed to settle and the supernatant liquid examined as to color. The following results were obtained:

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[1] Merck's reagent PbO_2 was employed throughout this work and was found to be free of manganese.

TABLE V.

	Result.
5 cc. = 5.0 mg. Mn	Deep purple
5 cc. = 2.5 mg. Mn	Deep purple
5 cc. = 0.5 mg. Mn	Deep purple
5 cc. = 0.25 mg. Mn	Purple
5 cc. = 0.125 mg. Mn	Purple
5 cc. = 0.05 mg. Mn	Pink
5 cc. = 0.025 mg. Mn	Faint pink
5 cc. = 0.005 mg. Mn	Very faint pink
5 cc. = 0.002[1] mg. Mn	Limit

The limit test shows a delicacy of one part in 2,500,000.

The influence of iron on the sensitiveness of the test was determined by the following procedure: varying mixtures of standard solutions of manganese chloride and iron chloride were precipitated with a slight excess of sodium hydroxide, the precipitates filtered and dissolved in a hot mixture of 0.5 cc. concentrated nitric acid and 4.5 cc. of water and finally treated with lead dioxide and boiled. The same results were also obtained with the solutions without precipitation, except that the salts used were $Fe(NO_3)_3.9H_2O$ and $MnSO_4.6H_2O$ in order to prevent the formation of *aqua regia*. The following results were obtained:

TABLE VI.

Parts Mn.	Parts Fe.	Result.
1 (0.02 mg.)	10	Good
1 (0.02 mg.)	20	Good
1 (0.02 mg.)	50	Good
1 (0.02 mg.)	100	Fair
1 (0.02 mg.)	200	Fair
1 (0.02 mg.)	300	Faint
1 (0.02 mg.)	400	Faint
1 (0.02 mg.)	500	Limit

The last result gave a nearly colorless solution. The effect of iron in discharging the color due to manganese recalls the use of manganese dioxide in glass manufacture. The absence of a yellow color when a large amount of iron is present might be taken to indicate its decolorization by the presence of manganese; it appears, however, that this cannot be depended upon for the reason that an iron solution of the concentration used in the limiting test was found to be decolorized by the lead dioxide and nitric acid treatment even when no manganese was present; hence, the nearly colorless solution obtained above is apparently not due to the mixture of the permanganate pink and the yellow iron.

It was thought desirable to make a few further tests to determin the influence of varying amounts of iron upon a larger constant quantity of

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[1] Noyes, Bray and Spear (THIS JOURNAL, 30, 556) have shown that the lead dioxide test is easily sensitive to 0.02 mg. Mn.

manganese than that employed above. The results obtained are given below:

TABLE VII.

Parts Mn.	Parts Fe.	Color.	Result.
1 (0.2 mg.)	500	Reddish pink	Good
1 (0.2 mg.)	1000	Reddish yellow	Fair
1 (0.2 mg.)	2000	Reddish brown	Doubtful[1]

From the results of Tables VI and VII it appears that the lead dioxide test for manganese is unreliable in the presence of three or four hundred parts of iron, unless a fairly large amount of manganese is present such as 0.2 mg. when a somewhat larger ratio of iron does not interfere with the test. On the other hand, the bead test is efficient with larger amounts of iron provided enough manganese (0.005 mg.) is introduced into the bead and provided the precautions cited under Table IV are followed.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, COLLEGE OF THE CITY OF NEW YORK.]

THE DETERMINATION OF THE SENSITIVENESS OF THE HYDROXIDE REACTIONS FOR THE COMMON METALS.[2]

BY L. J. CURTMAN AND A. D. ST. JOHN.

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The hydroxide reactions of the metals are perhaps the most common as well as the most important of those which take place in the wet way; yet no systematic work has been done to determin the delicacy of these reactions. The present work was therefore undertaken to supply this information, the need for which was felt in qualitative work. From the fact that the hydroxides studied were formed by precipitation, it might appear that the desired results could be calculated from the figures for the respective solubility products of the hydroxides; but it unfortunately happens that, with few exceptions, these figures have not as yet been determined; moreover, this information, even if available, would give but a rough idea of the sensitivity limit, for the reason that the final result of a sensitivity determination is largely an optical phenomenon that is controlled by factors, some of which are not included in the law of mass action. Chief among these factors are those which affect the visibility of the precipitate in very dilute solutions; such as its form, density, and color. In order to obtain comparable results, all the experiments were carried out under uniform conditions. The general procedure was as

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[1] The color given by the last test could not be readily distinguished from a solution containing 400 mg. of Fe as $Fe(NO_3)_3$ in 5 cc. It may also be noted that a solution of this concentration of iron was noticeably decolorized by the nitric acid and lead dioxide treatment.

[2] Read before Section I (Analytical Chemistry) of the Eighth International Congress of Applied Chemistry, September 11, 1912.