

GRAVIMETRIC DETERMINATION OF MANGANESE WITH 8-HYDROXY-QUINOLINE

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BERG¹ showed that manganese could be precipitated quantitatively by means of 8-hydroxy-quinoline ("Oxine") as a dull yellow crystalline compound having the molecular formula $Mn(C_9H_6ON)_2, 2H_2O$, which was very sensitive to acids. This author suggested two methods for the precipitation. In the first method, precipitation was carried out from a hot, neutral or weakly acid solution buffered by sodium acetate and containing a small amount of sulphite or hydroxylamine, by adding an excess of an alcoholic solution of oxine. Berg (*loc cit.*) pointed out that precipitation did not occur if the solution contained 6% acetic acid and that even a slight excess of acetic acid (0.3 to 0.5%) in the presence of a large excess of sodium acetate exerted a perceptible solvent effect. In the second method, to the hot solution containing a mineral acid and an excess of an acetic acid solution of oxine but no reducing agent, ammonia was added until weakly alkaline. The same author recorded that the precipitates obtained by both the methods could not be satisfactorily dried to constant weight since at 110° C. drying was very slow and above this temperature appreciable decomposition occurred. The gravimetric determination was, therefore, carried out by this author by igniting the precipitate to the oxide, Mn_3O_4 , with oxalic acid and weighing.

The conditions for the precipitation of the oxine complex have received attention from Taylor-Austin,² Hidehiro Goto,³ Tsinberg⁴ and Smith.⁵ The importance of pH is stressed by Goto (*loc cit.*). Tsinberg (*loc cit.*) states that neither hydroxylamine nor other reducing agent is necessary for precipitating the complex even from acetic acid solutions. However, it has been tacitly assumed by all investigators following Berg that the precipitates could not be dried to constant weight. Consequently these authors either completed the determination volumetrically or ignited the complex to the tetroxide.

Raikow and Tischkov⁶ have shown that the composition of the ignited tetroxide depends on the temperature and the nature of the atmosphere surrounding the precipitate during the ignition. It is obvious that this procedure is also defective in that no advantage is taken of the higher molecular weight of the oxine complex.

Although several methods for the gravimetric determination of manganese are available, it is well known that even the best among them, namely the phosphate method, requires a correction to be applied for the manganese escaping precipitation. It is, therefore, of considerable interest to re-investigate Berg's procedures.

PRELIMINARY INVESTIGATION

In the first series of experiments the precipitations were carried out according to Berg's first procedure. Drying was found to be very slow at 110° C. and at higher temperatures marked decomposition occurred as stated by Berg. To remove adsorbed oxine alcohol was used for the final washing. On drying the precipitates in an air oven, it was found that constant weight was quickly attained even at 110° C. and no decomposition occurred at 130° C. Tests carried out on the filtrates, however, indicated the presence of manganese. Since complete precipitation of the complex occurred only at pH 5.9 (Goto, *loc. cit.*) and alcohol is frequently acidic, it was concluded that washing with alcohol was not suitable though it facilitated drying. However, an important fact which emerged from these experiments is that contrary to the statement of Berg, manganese-oxine complex could be dried at much higher temperatures than 110° C. without decomposition. The present author is of opinion that a trace of manganese dioxide which may be formed under the conditions of precipitation by Berg's first method may oxidise the complex. Traces of aldehydes in the alcohol might reduce the oxide and thereby effectively prevent the decomposition. It is of interest to note in this connection that Tsinberg (*loc. cit.*) claims that no reducing agent is necessary during precipitation of manganese by oxine in acetic acid solution. Since this author ignites the precipitate to the tetroxide, the presence of manganese dioxide in the precipitate could not affect the results. A point which appears to support the above view is a fact noted by Smith (*loc. cit.*) that when a manganese solution containing both oxine and hydrogen peroxide is boiled for several minutes, a deep brown solution results. It was repeatedly observed by the present author that, when the complex was dissolved in hot dilute hydrochloric acid, a deep reddish brown solution was obtained. This seems to indicate that manganese-oxyquinolate is readily oxidised; no such decomposition was noticed in the solution of magnesium or aluminium oxine complexes. From the above considerations it appears that to avoid decomposition of the manganese-oxine precipitates during drying it is necessary to prevent precipitation of even a trace of manganese dioxide. From the results obtained in a number of experiments, it is concluded that Berg's first method of precipitation is unsuitable if the precipitate is to be dried to constant weight. The presence of a reducing

agent during precipitation apparently did not prevent precipitation of the dioxide.

The precipitates obtained by the second method gave satisfactory results on drying without any special treatment. Prolonged drying (20 hours) at 150° C. did not produce any decomposition; even at 170° C. no decomposition occurred. At much higher temperatures a slight discoloration was occasionally noticed but it was inappreciable in amount. Even this could be avoided by adding a few drops of sulphurous acid to the solution before precipitation. However, a temperature of 150° C. was considered to be the most suitable for drying. Constant weight was attained in two to three hours and the composition of the dried precipitate corresponded to $\text{Mn}(\text{C}_9\text{H}_6\text{ON})_2$ containing 16.03% manganese.

A series of experiments were performed to determine the best conditions for the precipitation and, as one of the objects of this investigation was to utilise the method for the determination of manganese in rock analysis, the effect of large amounts of ammonia, ammonium chloride, and sodium chloride was also investigated.

EXPERIMENTAL

Preparation and Standardisation of Manganese Solution

A solution of manganous chloride containing approximately 100 mg. of manganese in 50 c.c. was prepared from a pure sample of the salt. The manganese content was determined on an aliquot (50 c.c.) by conversion to and weighing as $\text{Mn SO}_4 \cdot \text{H}_2\text{O}$ according to the method of Brinkmann and Smedding.⁷ This method gave reproducible results and since only a pure solution of manganese was used, the figures were taken as standard. The results obtained are recorded in Table I.

TABLE I

No.	Mn $\text{SO}_4 \cdot \text{H}_2\text{O}$ obtained	Mn calculated	Deviation from mean
1	0.3295 g.	0.1072 g.	mg. + 0.2
2	0.3297	0.1072	+ 0.2
3	0.3284	0.1068	- 0.2
4	0.3289	0.1069	- 0.1

Mean value = 0.1070 g.

Oxine Reagent

A. R. quality oxine supplied by Messrs. B. D. H., London, was employed in this investigation. A 5% solution in acetic acid (2N) was prepared. This was diluted to 0.5% with the same acid when required.

Precipitation of Manganese as the Oxyquinolate

The procedure adopted was essentially the same as the second method of Berg.

An aliquot of the manganese solution (25 c.c.) was treated with 5–15 c.c. of hydrochloric acid (2N) and a small excess (0.5 to 1 c.c.) of the oxine reagent. The solution was diluted to 100 c.c., heated to 60–70° C. and the complex precipitated by adding ammonium hydroxide (2N) from a separating funnel until the solution was distinctly alkaline to litmus. The contents were then raised to the boil and the beaker left on the water-bath for half to one hour. The precipitate was then filtered through a weighed sintered glass crucible (No. 3 porosity), washed with hot water and dried to constant weight in an air oven which was thermostatically controlled at 150° C. Constant weight was attained in two to three hours. The manganese content of the weighed precipitate was calculated on the basis of complete dehydration (16.03% Mn). Typical results obtained are given in Table II.

TABLE II

No.	Manganese (taken)	Manganese (found)	Error
1	0.0535 g.	0.0534 g.	- 0.1 mg.
2	do	0.0534	- 0.1
3	do	0.0534	- 0.1

Influence of an Excess of Oxine

Calculation shows that 53.5 mg. of manganese require approximately 6.0 c.c. of 5% oxine acetate solution. In Table III are recorded results obtained by adding a measured excess of the precipitant, the other conditions being exactly as described above.

TABLE III

(Manganese taken = 0.0535 g.)

No.	Oxine solution in excess	Manganese (found)	Error
1	2.5 c.c.	0.0536 g.	+ 0.1 mg.
2	do	0.0536	+ 0.1
3	do	0.0536	+ 0.1
4	4.5 c.c.	0.0536	+ 0.1
5	do	0.0536	+ 0.
6	6.5 c.c.	0.0538	+ 0.3
7	do	0.0537	+ 0.2
8	9.5 c.c.	0.0541	+ 0.6
9	do	0.0541	+ 0.6
10	do	0.0540	+ 0.5

It is clear that satisfactory results are obtained in a single precipitation until nearly double the volume of reagent solution theoretically required is used and thereafter the results tend to become appreciably higher.

Double Precipitation

The first precipitation was carried out with 9.5 c.c. of the reagent in excess. The precipitate was filtered, washed and dissolved in hot hydrochloric acid (2N). A deep reddish brown solution was obtained. 1 c.c. of the reagent solution was added and the precipitation carried out with dilute ammonia as before. The results obtained are given in Table IV.

TABLE IV

No.	Manganese (taken)	Manganese (found)	Error
1	0.0535 g.	0.0540 g.	+ 0.5 mg.
2	do	0.0541	+ 0.6
3	do	0.0540	+ 0.5
4	do	0.0540	+ 0.5

Comparison of the results recorded in Tables III and IV shows clearly that when the first precipitation has been carried out with a large excess of oxine solution, the accuracy of the results could not be improved by a second precipitation. This is rather unusual and is probably connected in some manner with the production of deeply coloured solutions on dissolving the complex in acid.

Influence of Strong Ammonia

Precipitation was carried out in presence of an excess of the reagent by adding dilute ammonia and then 5 c.c. of strong ammonia (sp. gr. 0.88) was gradually added and the determination completed as before. Results obtained are recorded in Table V.

TABLE V
(Manganese taken = 0.0535 g.)

No.	Oxine solution in excess	Mn Found	Error
1	2.5 c.c.	0.0536 g.	+ 0.1 mg.
2	do	0.0536	+ 0.1
3	6.5	0.0538	+ 0.3
4	do	0.0538	+ 0.3
5	9.5	0.0549	+ 1.4
6	do	0.0548	+ 1.3

It is clear from the data recorded in the above table that when a large excess of oxine reagent is used along with strong ammonia, the values tend to be much higher than in the absence of strong ammonia.

Influence of Salts

Ammonium chloride (10 g.) or sodium chloride (15 g.) was dissolved in the manganese solution and the precipitation carried out with dilute ammonia after adding a small excess (1–2 c.c.) of the oxine reagent. The results obtained are recorded in Table VI.

TABLE VI
(Manganese taken = 0.0535 g.)

Salt added	Mn found	Error
Ammonium chloride ..	0.0535 g.	0.0 mg.
do ..	0.0536	+0.1
do ..	0.0535	0.0
Sodium chloride ..	0.0534	-0.1
do ..	0.0534	-0.1
do ..	0.0535	0.0

The results obtained show that large amounts of either ammonium chloride or sodium chloride have no influence on the accuracy.

Determination of small amounts of Manganese in presence of Sodium chloride

The solution for this determination was prepared by suitably diluting the original standardised solution. In all the cases recorded in the table below, sodium chloride (15 g.) was dissolved in the manganese solution, an excess of a 0.5% solution of oxine acetate added and the precipitation carried out exactly as described above with dilute ammonia. Finally 5 c.c. of strong ammonia was added. The precipitates were digested on the water-bath and cooled to the laboratory temperature. Experiments showed that the precipitates were finer grained than in previous cases and filtration should be carried out using No. 4 porosity sintered glass crucible. The precipitates were washed and dried as before. Typical results are recorded in Table VII.

TABLE VII

No.	Manganese (taken)	Manganese (found)	Error
1	4.0 mg.	4.1 mg.	+ 0.1 mg.
2	do	4.2	+ 0.2
3	2.7	2.7	0.0
4	do	2.8	+ 0.1
5	1.3	1.4	+ 0.1
6	do	1.4	+ 0.1
7	0.5	0.6	+ 0.1
8	do	0.6	+ 0.1
9	0.3	0.4	+ 0.1
10	do	0.4	+ 0.1

It may be noted that the conditions under which precipitations have been carried out are those which occur in the analysis of rocks if an attempt is made to precipitate magnesium and residual manganese together with oxine. Since the manganese in this mixture is determined colorimetrically, the above results should be regarded as quite satisfactory.

SUMMARY

Precipitates of manganese oxyquinolate obtained from a mineral acid solution containing a slight excess of oxine by adding dilute ammonia, according to Berg's second method, could be dried to constant weight at 150° C. and weighed. A slight superficial discoloration which may be observed in some cases is inappreciable even when dealing with small amounts of manganese. The composition of the dried precipitate corresponds to $Mn(C_9H_6ON)_2$ and contains 16.03% manganese.

Satisfactory results are obtained in a single precipitation provided a large excess of oxine is not added. A large excess of oxine with or without the addition of strong ammonia tends to yield higher results. Double precipitation does not improve the accuracy of the results in such cases.

The presence of large amounts of ammonium or sodium chloride does not appreciably affect the accuracy of the results.

Small amounts of manganese ranging from 0.3 to 4.0 mg. could be satisfactorily determined in presence of large amounts of sodium chloride and strong ammonia.

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