VOLUMETRIC DETERMINATION OF MANGANESE WITH 8-HYDROXY-QUINOLINE

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Berg[1] carried out the precipitation of manganese oxinate in two ways. In the first method, precipitation was carried out from an acetic acid-sodium acetate buffered solution containing a reducing agent by adding an alcoholic solution of oxine and in the second, the mineral acid solution containing manganese and oxine, without any reducing agent, was treated with dilute ammonia. The conditions for the precipitation of the complex were studied by Taylor-Austin,[2] Goto,[3] Tsinberg,[4] Smith[5] and Neelakantam.[6] The last author showed that the precipitates obtained by the second method could be dried to constant weight at 150° C., contrary to the statement of Berg, and recommended this method of precipitation.

The volumetric estimation was carried out both by the direct and indirect methods by Berg.[1] In the direct method the complex precipitated by one of the above methods was dissolved in hydrochloric acid and titrated bromatometrically in the usual manner. In the indirect method, the complex was precipitated by adding an excess (measured volume) of the reagent and the excess determined in the filtrate. Excellent results were recorded in both cases.

Neelakantam[6] reported that appreciable adsorption of oxine by the precipitate occurred when the precipitation was carried out in the presence of an excess of the reagent, with or without the addition of strong ammonia, and that a double precipitation did not improve the accuracy of the results in such cases. In the present investigation, the volumetric estimation of manganese under the conditions which occur in rock analysis was studied with special reference to the direct and indirect methods of titration suggested by Berg and their accuracies evaluated by comparison with the gravimetric method of Neelakantam.[6]

Experimental

Manganous Chloride.—Crystalline manganous chloride ($MnCl_2$, $4\,H_2O$; A.R.) was dissolved in water and acidified with hydrochloric acid to prevent hydrolysis. The stock solution was standardised by the oxine method

(gravimetric) proposed by Neelakantam[6] and the results checked up against the pyrophosphate method.

Oxine Solution.—A solution of oxine (2·5%) in acetic acid (2 N) was prepared.

Standard Bromate-Bromide (0·1 N).—Potassium Bromate (A.R. quality, 2·784 gm.) was accurately weighed out, dissolved in water along with potassium bromide (12 gm.) and made upto one litre.

Standard Sodium Thiosulphate (0·1 N).—Crystalline sodium thiosulphate (A.R. quality; 25 gm.) was dissolved in water and made up to one litre. The solution was standardised against the standard bromate solution in the usual manner.

Procedure: *Direct Method.*—The oxinate complex was precipitated according to the procedure recommended by Neelakantam.[6] In the volumetric method the precipitate was dissolved in hot dilute hydrochloric acid (2 N) and the liberated oxine determined bromatometrically in the following manner:—

The cold solution was treated with 3 drops of indigo carmine solution (1%) and titrated with standard bromate-bromide mixture slowly until the solution became pure yellow. The solution was diluted with 50 c.c. of dilute acid (2 N) and treated with 10 c.c. of potassium iodide solution (10%). The liberated iodine was titrated with standard thiosulphate, starch being added towards the end of titration.

The effect on the accuracy of the volumetric results of the following factors was investigated:—(*a*) magnitude of the excess oxine, (*b*) strong ammonia added after precipitation, and (*c*) presence of sodium chloride in large proportion.

Effect of Excess Oxine.—A measured volume of the oxine solution (2·5%) was added in excess of the theoretical requirement and precipitation carried out with dilute ammonia. Duplicate gravimetric and volumetric estimations were carried out. The results are given in Table I.

The results in Table I show clearly that both in the gravimetric and volumetric methods the errors are positive and tend to gradually increase with the excess oxine added. However, the volumetric method yields slightly higher values.

Effect of Strong Ammonia.—Precipitation was carried out using a slight excess (1 c.c.) of the reagent and dilute ammonia. Finally a measured volume of liquor ammonia was added. The determination was completed volumetrically. The results are given in Table II.

TABLE I

Manganese taken = 0·0575 gm.

No.	Oxine excess (c.c.)	Manganese Found (gm.)	
		Gravimetric	Volumetric
1	1·0	0·0575	0·0577
2	2·0	0·0578	0·0578
3	4·0	0·0578	0·0580
4	6·0	0·0579	0·0582

TABLE II

Manganese taken = 0·0575 gm.

No.	Liquor Ammonia (c.c.)	Manganese Found (gm.)	Error (mg.)
1	5·0	0·0580	+0·5
2	10·0	0·0581	-0·6
3	15·0	0·0583	+0·8
4	20·0	0·0585	+1·0

The above results show clearly that adsorption rapidly increases with the amount of liquor ammonia added.

Effect of Excess Oxine and Strong Ammonia.—Precipitation was carried out in presence of a measured excess of the oxine reagent by adding dilute ammonia and 20 c.c. of liquor ammonia was gradually added in each case. The determination was completed volumetrically. The results are given in Table III.

The adsorption of oxine is very strong. With excess of the reagent, the complex was obtained as a pasty mass which turned into a hard mass on boiling. Satisfactory washing of the precipitate was impossible.

TABLE III

Manganese taken = 0·0575 gm.

No.	Oxine excess (c.c.)	Manganese Found (gm.)	Error (mg.)
1	7·0	0·0585	+1·0
2	10·0	0·0593	+1·8
3	13·0	0·0594	+1·9
4	16·0	0·0625	+5·0

Effect of Sodium Chloride.—Precipitation was carried out in presence of 15 gm. of sodium chloride with a measured excess of oxine and dilute ammonia. The determination was completed volumetrically. The results are given in Table IV.

TABLE IV

Manganese taken = 0·0575 gm.

No.	Oxine excess (c.c.)	Manganese Found (gm.)	Error (mg.)
1	2·0	0·0574	−0·1
2	6·0	0·0575	Nil
3	10·0	0·0575	Nil
4	14·0	0·0582	+0·7

The above results compared with those given in Table I show clearly that the magnitude of the adsorption is lesser in presence of sodium chloride for the same excess oxine added.

From the above data it is clear that the direct titration method yields satisfactory results provided a large excess either of oxine or ammonia is not used in the precipitation.

Back Titration Method.—The manganese was precipitated under the conditions referred to above using a measured volume (excess) of a standard oxine solution from a burette. The precipitate was filtered through a

Whatman No. 41 paper and washed with hot water. The cold filtrate was made upto 500 c.c. in a measuring flask and aliquot portions titrated for excess oxine with bromate-bromide in the usual manner. The manganese content was calculated from the oxine used up. The results are given in Table V.

TABLE V

Manganese taken = 0·0575 gm.

No.	Oxine (c.c.)	Manganese Found (gm.)	Error (mg.)
1	19·0	0·0621	+ 4·6
2	23·0	0·0617	+ 4·2
3	27·0	0·0626	+ 5·1
4	31·0	0·0684	+10·9

The excess (over the theoretical requirement) of oxine used ranges from 6·5 to 18·5 c.c. in the above experiments. The errors are large, and this shows that the excess of oxine was not completely removed inspite of repeated washing. It was also noticed in the latter experiments that the precipitate was obtained as a pasty mass which became solid on heating. The magnitude of the excess used is normal to a back titration method. The back titration method is therefore unsatisfactory.

SUMMARY

The volumetric determination of manganese with 8-hydroxy-quinoline was investigated. Errors due to adsorption have been shown to increase with increase in (*a*) amount of excess reagent and (*b*) strong ammonia; and to decrease in presence of sodium chloride. The direct titration method was found to yield satisfactory results provided a large excess of oxine or ammonia was not used. The back titration method was found to yield very high values due to adsorption.

REFERENCES

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