DETERMINATION OF MAGNESIUM AND RESIDUAL MANGANESE IN ROCKS AND MINERALS WITH 8-HYDROXY-QUINOLINE

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Neelakantam[1] published recently procedures for the gravimetric determination of manganese, and of magnesia and residual manganese as they occur together in the analysis of rocks and minerals by means of 8-hydroxy-quinoline. In the latter case the manganese content was determined colorimetrically. Satisfactory results were obtained for both magnesia and manganese. This investigation was, however, carried out on pure solutions of the salts and the conditions obtaining in rock analysis were reproduced by adding oxalic acid, ammonium and sodium chlorides.

The present paper deals with the actual analyses of some rock and mineral samples, *viz.*, charnockite, leptynite and garnet by the above procedures and direct comparison of the results with those obtained by the usual pyrophosphate method.

Experimental

The finely ground sample (1·0 gm.) was weighed out accurately and opened up by fusion with sodium carbonate according to the procedure described by Harwood.[2] After eliminating the silica, the R_2O_3 hydroxides and lime and strontia, the filtrate was evaporated to dryness on the water-bath. The ammonium salts and oxalic acid were oxidised by means of concentrated nitric acid in the usual manner. The residue containing magnesia and the residual manganese was taken up in 5 c.c. of 2N hydrochloric acid and the solution made up to volume in a measuring flask (100 c.c.) with water. One aliquot (25 c.c.) was precipitated with ammonium phosphate according to standard procedure for Gibb's method[3] and the determination completed by ignition to the pyrophosphate and weighing. The manganese content of this residue was determined colorimetrically by the well known periodate method. An equal volume of the solution was precipitated with 8-hydroxy-quinoline according to the following procedure previously worked out by Neelakantam (*loc. cit.*).

To the solution containing magnesium and manganese, an excess of a 0·5% solution of oxine acetate (2N acetic acid) was added and heated to

60–70° C. Dilute ammonia was added dropwise with stirring until alkaline to litmus. Finally 3 c.c. of strong ammonia was added and the precipitate digested on the water-bath for one hour and cooled to laboratory temperature. The precipitate was filtered through a sintered glass crucible (No. 3), washed with hot dilute ammonia (1 : 40), dried to constant weight at 150° C. and weighed as anhydrous magnesium and manganese oxy-quinolinates. For the colorimetric estimation of manganese in this residue, the oxine complex was dissolved out in hot, dilute nitric acid, the solution evaporated to dryness in a platinum dish and the residue gently ignited to destroy the organic matter, moistening with concentrated nitric acid if necessary. The final residue was dissolved in a few drops of sulphurous acid, the manganese oxidised by periodate and nitric acid and estimated colorimetrically.

From the values obtained for manganese in both determinations, the magnesia contents were calculated by difference. The results are tabulated below:—

No.	Sample	MnO%		MgO%	
		Pyrophosphate Method	Oxine Method	Pyrophosphate Method	Oxine Method
1	Leptynite ..	0·05	0·09	1·82	1·80
2	Charnockite ..	0·07	0·09	9·01	9·02
3	Garnet ..	0·18	0·29	4·48	4·50

Discussion

It is to be noted that while the results obtained for magnesia by the two methods are in good agreement, the results for manganese by the oxine method of precipitation are definitely higher than by the pyrophosphate method. The explanation is to be found in the well known fact that the precipitation of manganese as the crystalline ammonium phosphate is generally incomplete, as much as 0·2 mg. or more escaping precipitation so that in accurate analyses it is customary to make final corrections based on colorimetric tests on the filtrate.[4] The oxine method obviously secures complete precipitation of residual manganese along with magnesia and gives more accurate results. The improvement is of considerable value in rock analysis, for the manganese content of the R_2O_3 is obtained by difference from the values for total and residual manganese and any error in its value reflects on the figure for alumina. Improved accuracy in the determination of

magnesia is also rendered possible by the oxine method as it is simple and the magnesium content of the anhydrous oxine complex is only 7·78%.

Summary

The magnesia and residual manganese have been precipitated together with oxine, the content of the latter determined colorimetrically and that of the former calculated by difference in the analyses of samples of charnockite, leptynite and garnet. The results obtained are compared with those obtained in parallel determinations carried out by the pyrophosphate method and improved accuracy in the estimation of residual manganese as well as magnesia claimed.

References

1. Neelakantam .. *Curr. Sci.*, 1941, 10, 20 (details under publication elsewhere).
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3. Gibbs, W. .. *Am. J. Sci.*, 1867, (II), 44, 216.
4. Hillebrand and Lundell .. *Applied Inorganic Analysis*, 1929, pp. 349.