121.—*8-Hydroxyquinoline as a Reagent for the Determination of Magnesium, especially in Carbonate and Silicate Rocks.*

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Magnesium has been precipitated with 8-hydroxyquinoline (" oxine ") in two ways : (i) by adding oxine to an ammoniacal solution containing ammonium chloride; (ii) by adding ammonia to an acid solution containing oxine. The former yields a purer precipitate, suitable for a gravimetric or a volumetric determination. The effect of heat on the precipitates has been examined at 105°, 140°, and 160°, and the dehydration of the dihydrated complex found to be accompanied by another subsidiary change. A standard method of precipitation, which gives excellent results gravimetrically in the determination of 10—50 mg. of magnesium oxide in 100 ml. of a solution free from foreign salts, except a little ammonium chloride, has been applied in a modified form to solutions containing ammonium oxalate and other salts, in quantities comparable with those obtained in the analysis of carbonate and silicate rocks, after the removal of silica, the " ammonia precipitate ", and calcium as oxalate. The results, corresponding to 25—1% of magnesium oxide, show errors that could be neglected in technical analyses, but not in accurate work.

Magnesium hydroxyquinolate (" oxinate ") may be quantitatively precipitated within the range of p_H 9·5—12·7 by two general methods : (i) a solution of 8-hydroxyquinoline (" oxine ") is added to an ammoniacal solution of the magnesium salt (Berg, *Z. anal. Chem.*, 1927, **71**, 23); (ii) ammonia in excess may be added to a neutral or slightly acid solution of magnesium containing oxine (Hahn and Vieweg, *ibid.*, p. 122). Berg separated and dried the precipitates at 105° [$Mg(C_9H_6ON)_2,2H_2O$] or 130—140° [$Mg(C_9H_6ON)_2$], obtaining " constant weight " after several hours' heating, or else dissolved them in hydrochloric acid, and determined the oxine volumetrically with a mixture of potassium bromate and potassium bromide. Hahn and Vieweg dried their precipitates at 140—160°. Kolthoff and Sandell (" Textbook of Quantitative Inorganic Analysis," 1936, 351) have adopted the second method of precipitation and recommend 105° as the drying temperature. In a review (*Z. anal. Chem.*, 1935, **101**, 303) favourable reference is made to the first method of precipitation, and a drying temperature of 140°. Redmond and Bright (*Bur. Stand. J. Res.*, 1931, **6**, 113), in a study of the precipitation of magnesium in solutions comparable to those obtained in the analysis of cements, employed both methods of precipitation, obtaining low or high results with the first, owing to two superimposed effects, *viz.*, a tendency to incomplete precipitation, and contamination of the precipitate by the reagent; and low results with the second, owing to a slow separation of the precipitate.

Oxine has been used in this analytical laboratory for more than six years in the determination of magnesium, and precipitation by the first method has given low results in the gravimetric, and high results in the volumetric process; precipitation by the second method has invariably given high results. Satisfactory weight constancy has not been readily achieved at 105°, 140°, or 160° with either method. In the application of the methods to dolomitic limestones the results obtained gravimetrically have compared favourably with those derived by determining magnesium as its pyrophosphate, but with silicates of small magnesium content some low, irregular results have been recorded. As the methods are comparatively rapid, we have sought to improve them by ascertaining the cause of the foregoing errors with a view to their eradication.

EXPERIMENTAL.

The Composition of Magnesium Oxinate.—Since precipitated magnesium oxinate may be contaminated with oxine, and the latter is volatilised on heating, a volumetric method of determining oxine was the best for examining the composition of freshly formed precipitates. The following method, based on the bromination procedures of Fleck, Greenane, and Ward (*Analyst*, 1934, **59**, 325) and Schulek and Clauder (*Z. anal. Chem.*, 1937, **108**, 385), was utilised. To the solution, 2N in hydrochloric acid (25 ml. and over), contained in a Pyrex flask, S 84, 1 g. of potassium bromide and 1 ml. of 0·01% aqueous methyl-red were added. It was slowly titrated with a 0·1N-potassium bromate solution until an excess of 1—2 ml. was present, as shown by the colour of the indicator. Carbon disulphide was placed in the funnel surrounding the stopper, and the flask kept for 5 minutes with occasional swirling. The solvent (8 ml.) was then added, followed, after vigorous shaking of the closed flask, by 2 g. of potassium iodide dissolved in a little water. The solution was back-titrated in the presence of starch with 0·025N-sodium thiosulphate solution, standardised against the bromate solution. By using the special flask, the loss of bromine, equivalent to 0·15 ml. of a 0·1N-solution, was prevented. With standard solutions containing 20—200 mg. of oxine, the method gave slightly low results on the average, and extreme errors of $\pm 0{\cdot}3\%$.

When magnesium oxinate (100 mg.) was precipitated according to the second method (see p. 656) and dissolved and determined volumetrically, positive errors of 1 and 8%, due to contaminating oxine, were recorded for experiments in which small (5%) and large (33 or 100%) excesses of oxine respectively were used. Considerable amounts of ammonium chloride and ammonium acetate reduced the errors, but more thorough washing of the precipitates did not materially help. When the first method of precipitation was similarly examined, small negative errors occurred, whether the excess of oxine was 10% or 50%, and the precipitates were apparently pure. An excess of 100% gave a positive error of only 0·6%. Large excesses of ammonium chloride and ammonia had no important influence.

In order to find how gravimetric determinations of magnesium would be affected by the two methods of precipitation, the action of heat on corresponding precipitates (of about 0·4 g.) was examined. With precipitates contaminated by 8% of oxine no satisfactory weight constancy was obtained at 105°, and the error after 3 hours was + 1·5%, whereas pure precipitates readily gave weight constancy and approximately correct results. The pure, dihydrated complex was converted into the anhydrous form in 2 hours at 140°, after which weight constancy was observed for short periods of heating. At 160° the conversion took about an hour and small losses in weight occurred on continued heating. Contaminated precipitates gave reasonable weight constancy in 2 hours at 160°, the results tending to be 0·5% high. The anhydrous precipitates were slightly hygroscopic, and from them a deep yellow substance was extracted with alcohol. This substance was not a product of decomposition of the anhydrous complex, but appeared to be formed to the extent of about 13% during the dehydration of the dihydrated complex. Probably it was 8 : 8′-diquinolyl ether, produced thus :

$$Mg(C_9H_6ON)_2,2H_2O \longrightarrow Mg(C_9H_6ON)_2,H_2O + H_2O \longrightarrow MgO + (C_9H_6N)_2O + H_2O$$

The simultaneous production of magnesium oxide might account for the hygroscopic nature of the supposed anhydrous oxinate.

The foregoing results show that, for volumetric and gravimetric determinations, magnesium oxinate is best precipitated by adding oxine last to an ammoniacal solution containing magnesium. For oxine-free precipitates the most satisfactory temperature of drying is 105°, but for oxine-contaminated precipitates a temperature of 160° leads, on the whole, to better results.

The Determination of Magnesium with Oxine.—Gravimetric and volumetric determinations of magnesium were made in solutions containing various amounts of a magnesium sulphate solution standardised according to Epperson's procedure (*J. Amer. Chem. Soc.*, 1928, **50**, 321). The standard method adopted for gravimetric experiments was as follows. To 100 ml. of a solution, containing the equivalent of 10—50 mg. of magnesium oxide, 2 g. of ammonium chloride, and 0·5 ml. of *o*-cresolphthalein indicator (0·02% in alcohol), 6N-ammonia was added in at least 2 ml. excess of that required to give a violet colour (p_H 9·5). The solution was heated to 70—80°, and, according as the amount of magnesium was large or small, a 5% or 1% solution of oxine in acetic acid (2N and 0·4N respectively) was added *very slowly*, with constant stirring, until the precipitation was complete and a *small* excess was present, as shown by the deep yellow colour of the supernatant liquid. At first, 2N-ammonia was added simultaneously with, and in amount equivalent to the acid in the oxine solution, but in later work a larger excess of 6N-ammonia was added before the oxine. The precipitate was digested for 10 minutes on the steam-bath, and filtered off hot on a Jena-glass filtering crucible (No. 10 G 4), the filtrate being used to complete the transference of the precipitate to the crucible. A trace of sodium tauroglycocholate in the solution reduced the tendency of the precipitate to adhere to the sides of the beaker (Hopkin and Williams, " Organic Reagents for Metals," 1938, 67). Finally, the precipitate was washed with 50 ml. of hot water, and dried at 105° or 160° for 1 hour, and then for ½-hour periods.

For single volumetric determinations of magnesium, within the same limits of concentration, all the foregoing quantities were reduced to one-fourth, with the exception of the wash liquid, which was halved. The precipitates were collected on No. 590 Whatman filter papers, dissolved in hot 2N-hydrochloric acid, and determined, as outlined on p. 656, with potassium bromate. If several titrations were required, a larger volume of the magnesium solution was taken, as in the gravimetric experiments, the precipitate dissolved in 2N-hydrochloric acid, and suitable portions of the solution were used. When the concentration of the magnesium oxide was less than 10 mg. per 100 ml., 100 or 200 ml. of the solution were taken. As the precipitates formed in such dilute solutions were finely divided and separated slowly, they were digested for a longer period and cooled for 1—2 hours before filtration. It was impossible to restrict the amount of oxine added to a small excess.

The results of a number of gravimetric and volumetric experiments are given below.

Gravimetric (initial vol. 100 ml.).
Wt. of MgO (mg.).

Taken.	Found. 105°.	Found. 160°.
(Small excess of oxine.)		
51·34	51·35	51·35
20·56	20·53	20·65
10·31	10·32	10·27
(100% excess of oxine.)		
51·34	51·53	51·38

Volumetric.

Initial vol., ml.	Wt. of MgO (mg.). Taken.	Wt. of MgO (mg.). Found.
25	12·83	12·79, 12·79
	5·14	5·16, 5·16
	2·58	2·63, 2·62
100	12·83	12·85 *
200	12·83	12·96 *
100	2·58	2·67 *
200	2·58	2·59 *

* Filtered cold.

The above figures show that, for concentrations of magnesium oxide ranging from 10 to 50 mg. per 100 ml., the most consistent results are obtained gravimetrically by weighing the dihydrated complex (105°). If, however, too large an excess (100%) of oxine has been added, drying should be effected at 160°. Volumetrically, the errors are irregular, and most of the precipitates appear to have been contaminated with a little oxine. The following factors were found not appreciably to influence the volumetric determination of larger amounts of magnesium, *viz.*, the amounts of ammonia added beyond a p_H value 9·5, the period of digestion before filtration, mechanical stirring, and the temperature of the filtered mixture. Large amounts of ammonium chloride and a 100% excess of oxine slightly raised the results. The solvent effect of hot water on the precipitates was about 0·09 mg. per 100 ml., and of hot N-ammonia, 0·07 mg. The former was preferred.

The Determination of Magnesium in Carbonate and Silicate Rocks.—When 1 g. of a carbonate rock is analysed according to the method given by Kolthoff and Sandell (*op. cit.*, pp. 356—360; 337), the solution, before the determination of magnesium, contains about 20 g. of ammonium chloride, and 4—2 g. of ammonium oxalate, according as the amount of magnesium to be separated from calcium is large (20% MgO) or small (<2% MgO). In the analysis of 1 g. of a silicate rock, fused with 5 g. of sodium carbonate, there remain in the solution, after successive removals of silica, the " ammonia precipitate ", ammonium salts, and calcium, 8 g. of sodium nitrate, 7 g. of ammonium chloride and 2 g. of ammonium oxalate, it being assumed that only moderate amounts of calcium and magnesium are present (Washington, " The Chemical Analysis of Rocks," 1930, pp. 148 *et seq.*, 175, and 202).

In order to test the applicability of the oxinate method to the determination of magnesium in the above minerals, magnesium sulphate corresponding to 25—1% of magnesium oxide was added to synthetic mixtures of the composition cited. It was supposed that, for amounts of magnesium oxide between 25 and 5%, one-fifth of the filtrates from the calcium oxalate precipitates would be taken, the volume being 100 ml., and, for 5—1%, the whole of the filtrates, concentrated to 200 ml. The concentrations of magnesium oxide to be considered were therefore 50—5 mg. per 100 ml. Since, with magnesium sulphate solutions containing minimal amounts of ammonium chloride, the greater part of this range was most successfully covered by gravimetric determinations of magnesium at 105°, the standard method then adopted (p. 657) was first applied, with the results shown in the third column of the table on p. 659.

Oxalate was found to retard the precipitation of even the maximum amount of magnesium, so that the precipitation began only after a few ml. of the reagent had been added, and then proceeded fairly quickly. Consequently, it was possible, after some practice, to control the excess of oxine added, when the amount of magnesium was large, but not when it was small. As the negative errors pointed to incomplete precipitation, the standard procedure for oxalate-free solutions was modified by cooling the mixtures for 1—2 hours before filtration, and mechanically stirring, for 15 minutes, solutions of low magnesium content (MgO$\sim$1%), from which the precipitates sometimes separated very slowly. As shown in the table, results of moderate accuracy were then obtained only when the precipitates were heated at 160°. Apparently the precipitates were impure and required to be heated at the higher temperature found more suitable for these (p. 657).

Wt. (g.) of mineral to which experiment refers.	MgO (%) under consideration.	Standard method, 105°.	MgO (%) found. Modified method,	
			105°.	160°.
Carbonate rock.				
0·2	25·00	24·91	24·85 †	24·92
0·2	5·00	4·94	5·08	4·99
1	1·00	—	—	0·98, 1·05 *
Silicate rock.				
1	5·00	4·88	5·06	4·97
1	1·00	0·87	—	0·91, 1·03 *
Dolomite No. 88.				
0·2	21·48 ± 0·06 ‡	21·15	—	21·31
Argillaceous limestone No. 1a.				
1	2·19 ‡	—	—	2·16 *

* Stirred mechanically after cooling. † Weight constancy difficult to obtain.

‡ U.S. Bureau of Standards' value.

As a further check on the method, a dolomite and a limestone from the U.S. Bureau of Standards were analysed for magnesium oxide. 1 G. portions, dried at 105°, were decomposed with hydrochloric acid and the insoluble residues removed. As the residue in the limestone was large, it was ignited, treated with hydrofluoric acid to expel silica, fused with a little sodium carbonate, dissolved in hydrochloric acid, and the solution added to the filtrate from the original residue. Iron, aluminium, and manganese were precipitated twice as the hydroxides, and calcium twice as calcium oxalate, according to standard methods (Kolthoff and Sandell, *op. cit.*). In the dolomite analysis one-fifth of the filtrates from the calcium oxalate precipitates was taken for the determination of magnesium, and, in the limestone analysis, the whole solution, evaporated to 200 ml. The results shown are considered satisfactory in view of the large number of separations that preceded the isolation of the magnesium.

Amounts of magnesium oxide under 1% could not be determined in the presence of ammonium oxalate, which would have to be destroyed in rock analysis. The solution left after its destruction by evaporation with concentrated nitric acid would be free from foreign salts in a limestone analysis, and would contain 8 g. of sodium nitrate in a silicate analysis. As this amount of sodium nitrate in 100 ml. of solution was found not to interfere with the determination of small amounts of magnesium, the method outlined on p. 658 for concentrations of magnesium oxide under 10 mg. per 100 ml. could therefore be applied.

As a whole, our work, like that of Redmond and Bright (*loc. cit.*), shows that the precipitation of magnesium oxinate is very susceptible to the manner in which it is carried out, and to the conditions prevailing in the solution. In the determination of magnesium in silicate and carbonate rocks the presence of oxalate causes most trouble. Oxalate may, of course, be destroyed, but the main benefit of using oxine as a precipitant, *viz.*, time-saving, is then lost. Our conclusion is that, in the determination of magnesium in the presence of oxalate, the reagent, if used in the manner prescribed (pp. 657, 658), quickly gives serviceable results, which, however, lack precision.

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