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DOLOMITE AND MAGNESITE WITH REFERENCE TO THE SEPARATION OF CALCIUM AND MAGNESIUM.

BY NICHOLAS KNIGHT AND WARD H. WHEELER.

The estimation of calcium and magnesium in a mineral or rock is frequently necessary and seems like a simple matter, yet a great deal of work has been done on the subject, and different views are held as to the best procedure. The method that he has become accustomed to is doubtless the best for the individual analyst or teacher. Some of the methods, however, seem to be more simple and direct, and therefore less likely to lead to error than other processes which have been devised.

*Richards developed a method for the separation of calcium and magnesium where the substances are somewhat equal in amount, as in dolomite, and his method differs in some important particulars from those commonly employed.

To the solution of calcium and magnesium chlorides, Richards adds three grams of ammonium chloride, then oxalic acid and sufficient hydrochloric acid to keep the calcium in solution. A drop of methyl orange solution is next added as an indicator, and dilute ammonia slowly, with constant stirring to alkaline reaction. Lastly an excess of ammonium oxalate is added.

In applying this method, we found some difficulty in getting all the magnesium precipitated. Indeed four successive crops were obtained. This was doubtless due to the large amount of ammonium oxalate employed. One advantage claimed for it is the small amount of magnesium precipitated with the calcium, which in two determinations was:

1. .0011 Mg O equivalent to .42 per cent of the whole.
2. .0013 Mg O equivalent to .54 per cent of the whole.

Average .48 per cent of the whole.

In our experiment with this method we obtained .0028 Mg O equivalent to 1.24 per cent of the whole.

By what seems to us a simpler method, which will be explained later we found only .08 per cent MgO equivalent to .37 per cent of the whole, and in a number of instances we obtained .11 per cent MgO equivalent to .51 per cent of the whole.

We afterwards repeated the experiment and obtained .13 per cent. On re-dissolving this and re-precipitating we found only .01 per cent. A second time we obtained only .07 per cent, which when re-dissolved and re-precipitated gave no residue, and a third time we found no magnesium had precipitated.

*Zeitschrift für Anorg. Chemie July, 1901.

(1). Wolcott Gibbs conducted a series of experiments by which he concluded that it is more convenient to precipitate magnesium from a boiling concentrated solution with microcosmic salt instead of in the cold with disodium phosphate. The mean of four determinations with pure crystallized magnesium sulphate was .06 2-3 per cent. too high in MgO. While by the addition of ammonium chloride, it was reduced to .03 1-3 per cent. too high. Two analyses were next made by precipitating the boiling solution of disodium phosphate, after the addition of ammonium chloride. The result was .58 per cent, too high in MgO. When the precipitate thus obtained was dissolved in hydrochloric acid and re-precipitated with ammonia, the result was only .05 per cent, too high in MgO.

(2). Gooch and Austin conducted a valuable series of experiments, the object of which was to determine when results too high in magnesium are obtained, whether such results are due to mechanical occlusion in the crystalline phosphate, or to a variation in the magnesium ammonium phosphate, obtaining a product richer in ammonia and poorer in magnesium. They used microcosmic salt as the precipitant and obtained a salt $(\text{NH}_4)_4\text{Mg}(\text{PO}_4)_2$ to a greater or less extent with the ideal magnesium ammonium phosphate, MgNH_4PO_4 , which would give a result too high in magnesium. To obtain the ideal salt, the first precipitate must be dissolved in hydrochloric acid and re-precipitated with ammonia. The authors commend the method of Gibbs of using microcosmic salt as the precipitant, and claim that by boiling the solution from three to five minutes the ideal salt is readily obtained.

We have repeated the separation of calcium and magnesium by the method described on page 127 of the Proceedings of the Iowa Academy of Sciences of the Year 1903, and still commend its accuracy and simplicity. The solution of ammonium oxalate was prepared by dissolving 10 grams of the purest obtainable crystals in 275cc of distilled water. The amount in a cubic centimetre was thus easily known. To insure the greatest possible accuracy, the precipitant should not be taken from a stock solution, but should be made up as required, on account of the solvent action upon glass. The solutions of calcium and magnesium chlorides were heated to boiling and kept at that temperature while the theoretical amount of the ammonium oxalate solution necessary to precipitate the calcium was added, and then two to four centimetres additional. After standing at least eight hours, the precipitate was filtered off. The filtrate was tested with one or two centimetres of the ammonium oxalate solution to learn if all the calcium was precipitated which was usually found to be the case. We thus learned that it did not seem necessary to add sufficient ammonium oxalate to change all the magnesium chloride into oxalate on account of the supposed solubility of calcium oxalate in magnesium chloride. It is doubtless true that in precipitating magnesium an excess of ammonium oxalate does no harm, contrary to the teaching of some of the text-books, but an excess of ammonium salts simply retards the precipitation of magnesium. It is therefore unnecessary to remove the ammonium salts by heat before precipitating the magnesium.

1. Am. J. Science 3. 5. 114. 1873.

2. American J. Science 4. 7. 187. 1899.

The precipitate from the ammonium oxalate, consisting of the calcium and possibly a small amount of magnesium need not be washed as the small quantity of magnesium that is present will not be precipitated a second time with the calcium. For the same reason in a specimen of rock where the calcium is greatly in excess of the magnesium, a second precipitation is not necessary.

In the case of dolomite, the precipitate is dissolved on the paper with a small quantity of warm dilute hydrochloric acid, and the calcium is a second time precipitated with ammonia and a little ammonium oxalate, the magnesium now remaining in solution. The filtrate can be added to the main filtrate which contains the bulk of the magnesium. These filtrates should be concentrated if necessary. Care must be exercised in washing the precipitated calcium oxalate, which we have found to be appreciably soluble in hot water, less so in cold water, but it is best washed in cold water, to which a little ammonium oxalate has been added. On account of this solubility, it is better to wash the calcium oxalate on the filter rather than by decantation. In the analysis of Iceland Spar, washing the precipitated calcium oxalate is unnecessary as there are present with the precipitate only ammonium salts which the heat will afterwards volatilize.

The somewhat concentrated filtrate containing the magnesium is precipitated, while cold with a solution of disodium phosphate with constant stirring, and about 25cc. of ammonia water is added. It is allowed to stand 24 hours before filtering. *Lawrence Briant found that by violently shaking for ten minutes in a stoppered bottle all would be precipitated. Time, however, is not usually an object in such analyses, as other work can be in progress while the precipitate is standing.

Should there be present with the normal magnesium ammonium phosphate more or less of the other salt $(\text{NH}_4)_4\text{Mg}(\text{PO}_4)_2$, it would only be necessary to dissolve in hydrochloric acid and re-precipitate with ammonia.

We have found in hundreds of analyses of pure magnesium sulphate that very seldom do we get too high a result by precipitating as before described with disodium phosphate, and the same appears to be true of dolomite, although in the latter substance it is more difficult to know what is the real content. The occasional high result can be explained by imperfect washing of the precipitate.

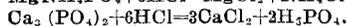
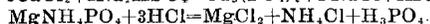
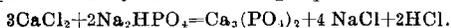
In estimating the phosphoric acid in disodium phosphate with "magnesia mixture", the average student will more frequently obtain too high a result, but this seems to be the case when a large excess of the mixture has been carelessly added and the precipitate has been imperfectly washed. Our experience on the whole would tend to show but little necessity for a second precipitation.

Microcosmic salt is considerably more expensive than disodium phosphate, but doubtless the difference in the cost would ordinarily not be considered.

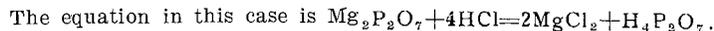
*Crooks Select Methods, page 51.

Concerning the small amount of magnesium that may come down with the calcium; the usual washing of the precipitate with hot water might remove an amount of calcium equal to the weight of the precipitated magnesium, and this amount would be afterwards precipitated with the magnesium. One source of error might almost completely balance the other and a satisfactory result would thus be easily attained. However, we do not practice or advocate such a procedure.

Treadwell-Hall in their work on quantitative analysis, page 71, call attention to an error quite often made by beginners. If all the calcium is not precipitated, it will come down with the magnesium and the total result will be too low. In order to separate the calcium from the mixture of the two phosphates, the precipitate after standing 12 hours is filtered, washed, dissolved in a small quantity of hydrochloric acid, and ammonia is added until the solution is alkaline. It is then strongly acidified with acetic acid, heated to boiling and precipitated with a boiling solution of ammonium oxalate. After 12 hours, the calcium oxalate is filtered, washed with hot dilute acetic acid and determined as calcium oxide. The filtrate is evaporated to dryness, the ammonium salts driven off, the residue dissolved in a little dilute hydrochloric acid and precipitated as usual. The reactions involved are represented by the following equations:



The acetic acid prevents any precipitation either of the calcium or magnesium until the ammonium oxalate is added to precipitate the calcium. If the magnesium ammonium phosphate is changed to the pyrophosphate, the acetic acid does not prevent the precipitation of the magnesium and the separation cannot be effected.



The equation is similar for calcium.

The pyrophosphoric acid slowly adds water and becomes $\text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O} = 2\text{H}_3\text{PO}_4$.

The occlusion of ammonium oxalate by calcium oxalate.

In a private communication from Dr. Gregory P. Baxter, of Harvard University, he states that he has not published the results of his research upon the occlusion of oxalic acid and ammonium oxalate by calcium oxalate and that his results though somewhat unsatisfactory, pointed to no appreciable occlusion. Our test was as follows: We removed ammonia from a flask and Liebig condenser by distilling water through for an hour, or until the distillate gave no color with Nessler reagent. Then we added the well-washed calcium oxalate precipitate from a gram of the dolomite to the flask with 500 cc. of distilled water and 50cc. of alkaline permanganate solution. 300cc. were distilled off and 50cc. of the distillate gave scarcely a trace of color with Nessler solution. The same result was obtained whether the calcium oxalate was tested before drying, or whether it had been heated strongly with the blast lamp. The oxalate had been slowly precipitated from a boiling solution by constant stirring.

If one looks for all the substances that have been found in dolomites, free and combined water, organic matter, alkalis S. SO_3 , TiO_2 , P_2O_5 , SrO and BaO , these in addition to the silica, ferrous and ferric iron, and alumina, and determines all the constituents present, it would constitute a somewhat complicated analysis, and would afford a large variety of practice.

The estimation of the carbon dioxide by the Bunsen method continues in favor in our laboratory. The amount of carbon dioxide obtained in the specimen of argillaceous limestone, which was the subject of the co-operative analysis by the two government officials was 30.59 per cent. and 30.77 per cent. One of our students obtained 30.76 per cent. before the results were published in the February number of the Journal of the American Chemical Society.

Magnesite—

A. The calcium was precipitated according to the method of *Scheerer. A half gram of the powdered mineral was changed to the sulphate. Alcohol was added to the aqueous solution until a persistent cloudiness was produced. After standing some hours all the calcium sulphate is precipitated. If too much alcohol has been added, some of the magnesium sulphate will also be precipitated, in which case the two sulphates are dissolved in water and the calcium is precipitated with alcohol or with ammonium oxalate.

B. The magnesite was dissolved in hydrochloric acid and an attempt was made to precipitate the calcium with ammonium oxalate, and making a double precipitation. There was obtained .23 per cent of calcium oxide more by method A than by B. It is evident, therefore, that when the amount of magnesium is relatively large method A is to be preferred.

An analysis of the magnesite resulted:

MgCO_3	98.43	per cent.
CaCO_3	1.22	per cent.
SiO_2	0.19	per cent.
	<u>99.84</u>	per cent.

The specimen was purchased of the dealers and its locality was not ascertained.

*Crooks Select Methods, page 52.