ium, the latter can be obtained in the least soluble portion and in this respect differs from nearly all the other methods for its separation.

In conclusion, it may be as well to mention that the third part of this paper will appear shortly. We also acknowledge our indebtedness to the Welsbach Company for material supplied for future investigation through the courtesy of Dr. H. S. Miner.

NEW HAMPSHIRE COLLEGE, DURHAM, N. H.,
June 9, 1909.

THE QUANTITATIVE SEPARATION OF CALCIUM FROM MAGNESIUM.

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Received June 2, 1909.

Although methods for the separation of these elements, which depend upon the relative solubilities of their carbonates, chromates and sulphates, respectively, have found advocates, none of these possess decided advantages over the more generally used oxalate process. The theory of the last-mentioned method has been discussed by Richards, McCaffrey and Bisbee,[1] who also determined the magnitude of the error resulting from the occlusion of magnesium by the precipitated calcium under a series of varying conditions. These experiments showed that this error could be greatly reduced by precipitating with oxalic acid from a slightly acid solution and subsequent neutralization, rather than by precipitating with ammonium oxalate from an alkaline solution according to the usual method. A somewhat extended use of the newer method has in general given excellent results, but as the experiments referred to were practically limited to cases in which approximately equivalent amounts of calcium and magnesium were present, and as the method seemed to be, for many practical purposes at least, unduly elaborate, it seemed desirable to secure further experimental data with regard to its more general application.

Limitation of the Problem.—In taking up the further study of the method its practical application to the conditions usually met with in analytical work was constantly kept in mind. In order to render the problem a definite one it was assumed that the substance to be analyzed might vary continuously in composition from pure calcite to pure magnesite, and that the amount used for the analysis was 0.6 gram. It was further assumed that chlorine was the only negative ion present in the solution, that the latter in every case contained 3.5 grams of ammonium chloride and was heated to boiling and diluted to 300 cc. before the precipitant was added. These limitations were adopted partly as the result of practical considerations and partly as the result of previous experience with the method. There are three main sources of error to be considered.

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[1] *Proc. Am. Acad. Arts Sci.*, **36**, 375 (1901).

Error Resulting from Precipitation of Magnesium Oxalate.—The investigations of Kohlrausch[1] have shown that magnesium oxalate possesses a number of remarkable properties. Although its normal solubility was found to be 0.3 g. per liter it was found possible, when working below 18°, to prepare solutions containing three hundred times this amount of dissolved salt. Although long standing or agitation slowly precipitated the excess, solutions containing nearly forty times the normal amount, that is 11.75 g. per liter, were comparatively stable, and even after standing for three weeks contained one and one-half times the normal amount of dissolved salt. A further peculiarity of these solutions was the slight extent to which the dissolved salt was dissociated; only about ten per cent. of the salt in the solution containing 11.75 g. per liter was in the dissociated condition, and in the solution containing 0.3 g. per liter only about one-third of the dissolved salt was ionized.

It is not possible to calculate with even approximate accuracy the solubility of magnesium oxalate under the conditions which actually prevail in making this separation; it should greatly exceed the normal value owing to the formation of complex ions with the ammonium salts present, but should be reduced somewhat by the excess of precipitant commonly used. A series of qualitative experiments, in which solutions containing definite amounts of magnesium chloride and varying amounts of ammonium chloride were used, established the fact that both of these factors influenced profoundly the point at which the saturation limit was reached. A solution containing magnesium oxalate corresponding to 0.35 g. of the oxide in a volume of 300 cc., and therefore representing one extreme of the conditions here being considered, would have a concentration nearly ten times as great as that of a normally saturated solution. Although the presence of 3.5 g. of ammonium chloride should greatly increase this solubility it was found that solutions of this composition were in reality supersaturated. The degree of supersaturation was not sufficient to bring about precipitation unless the solution was continuously stirred and heated, or unless allowed to stand for twenty-four hours. Students making this separation in the laboratory, under conditions approximately equivalent to those described above, have frequently obtained a partial separation of the magnesium, but only where the solution was allowed to stand over night. The separated magnesium oxalate may be recognized by the characteristic crystalline crust which it forms. Attempts were made to reduce the probability of error from this source by the introduction of ammonium salts of various organic acids; of these the citrate was the most effective but unfortunately

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[1] *Ber. Preuss. Akad.*, **39**, 1223 (1904).

it also retarded the precipitation of the calcium and its use was finally abandoned.

Error from Incomplete Precipitation of the Calcium.—The solubility of pure calcium oxalate, as determined by Richards (*loc. cit.*), amounts to 6.8 g. per liter at a temperature of 25° and the amount of precipitate dissolved by 300 cc. of water might therefore amount to 2 mg. The presence of ammonium chloride might be expected to increase the error from this source somewhat, but quantitative data upon this point are lacking. The error is certainly large enough to suggest the desirability of reducing the solubility of the precipitate by the addition of an excess of the precipitating agent employed.

The presence of magnesium in the solution introduces a further difficulty. Owing to the slight extent to which magnesium oxalate undergoes dissociation, much of the precipitant added may be used up in the formation of non-dissociated magnesium oxalate and the concentration of the C_2O_4 ions reduced thereby to such an extent as to prevent complete precipitation of the calcium. The equilibrium existing between non-ionized magnesium oxalate and insoluble calcium oxalate is an important factor in the completeness of the precipitation, and is the source of the error noted by Fresenius and ascribed by him to the solvent action of magnesium chloride on calcium oxalate. The use of a large excess of precipitant should overcome this error and the rule adopted by Fresenius was to add sufficient precipitant to combine with both the calcium and magnesium present. It may be calculated from the determinations of Kohlrausch (*loc. cit.*) that about one-half the salt in a solution containing magnesium oxalate equivalent to 0.35 g. of magnesium oxide in 300 cc. is in the dissociated condition, and even disregarding the fact that much of the magnesium probably exists in the form of complex magnesium-ammonium ions, the amount of precipitant recommended would seem to be somewhat excessive. The presence of large amounts of magnesium salts also have the effect of delaying the precipitation of the calcium and makes it necessary either to use a large excess of precipitant or to allow the solution to stand for a longer time than would otherwise be necessary.

In order to determine definitely the amount of precipitant needed to effect complete precipitation of calcium in the presence of large amounts of magnesium, measured amounts of carefully standardized solutions of pure calcium and magnesium chlorides were precipitated in Jena glass beakers. Each solution contained 3.5 g. of ammonium chloride and was heated to boiling and diluted to 300 cc. before precipitation. Precipitation was effected by adding a solution of oxalic acid and then making alkaline by the gradual addition of a dilute solution of ammonium hydroxide. The precipitate was allowed to stand for an hour, then collected and weighed; it was then dissolved in a small amount of hydrochloric acid and the calcium again precipitated and weighed under the same conditions as before, except that the volume and amounts of ammonium salts used were reduced in proportion to the amount of precipitate. In some instances the magnesium remaining in the solution after the second precipitation of the calcium was also determined.

No. of experiment.	I.	II.	III.	IV.	V.
Wt. of CaO used	0.0350	0.0350	0.0350	0.0350	0.0350
Wt. of MgO used	0.3500	0.3500	0.3500	0.3500	0.3500
Wt. of $(COOH)_2 2H_2O$ added	0.2500	0.6250	1.0000	1.250	1.250
Wt. of first ppt	0.0279	0.0319	0.0369	0.0395	0.0404
Wt. of second ppt	0.0271	0.0311	0.0304	0.0350	0.0344
Wt. of MgO in filtrate	....	....	....	0.0039	0.0045

In Experiment I the precipitant added was sufficient to combine with all the calcium and one-seventh of the magnesium yet only about eighty per cent. of the calcium was precipitated. In Experiment II sufficient precipitant to combine with all the calcium and about one-half the magnesium was used and about ninety per cent. of the former was precipitated. In Experiments III, IV and V more than enough precipitant to combine with all the calcium and magnesium was added; here the precipitation was complete but a positive error due to occluded magnesium appears.

Error from Occlusion.—The work of Richards established the fact that the amount of occluded salt depends upon the amount of non-dissociated magnesium oxalate in the solution at the time during which the calcium precipitate is separating and may be reduced by any cause which reduces the concentration of the C_2O_4 ions present. His investigation led him to recommend that sufficient oxalic acid to combine with all calcium present be first added to the neutral or slightly acid solution, that ammonium hydroxide sufficient to make the solution alkaline be added very slowly (consuming a half hour in the addition), that a large excess of ammonium oxalate be next added, that the precipitate be allowed to stand for four hours, and then filtered and washed with a solution of ammonium oxalate.

Although the results obtained by following these instructions are very satisfactory, the amount of time and labor involved in its execution are so great that the method possesses but little advantage over the method of double precipitation usually employed. The specification as to the total amount of precipitant, that is of oxalic acid and ammonium oxalate, is indefinite and the very gradual addition of the ammonium hydroxide is of little significance in those cases in which the amount of magnesium is large, for under these circumstances the calcium does not begin to precipitate until the neutralization is practically complete.

In the experiments which are tabulated below, the method of Richards was modified by adding the specified amount of oxalic acid, neutralizing the solution with a one per cent. solution of ammonium hydroxide, added within a period of five minutes, allowing the precipitate to stand for one hour only, and omitting the further addition of ammonium oxalate to either solution or wash water.

No. of experiment.	IV.	VI.	VII.	VIII.	IX.
Wt. of CaO used	0.0350	0.1400	0.2100	0.2800	0.3500
Wt. of MgO used	0.3500	0.2800	0.2100	0.1400	0.0350
Wt. of $(COOH)_22H_2O$ added	1.2500	1.2500	0.2500	1.2500	1.2500
Wt. of first ppt	0.0395	0.1431	0.2113	0.2801	0.3490
Wt of second ppt	0.0352	0.1398	0.2098	0.2789	0.3487
Wt. of MgO in filtrate	0.0039	0.0027	0.0025	....	....

No. of experiment.	X.	XI.	XII.	XIII.	XIV.
Wt. of CaO used	0.0350	0.1400	0.2100	0.2800	0.3500
Wt. of MgO used	0.3500	0.2800	0.2100	0.1400	0.0350
Wt. of $(COOH)_22H_2O$ added	1.000	1.000	1.000	1.000	1.000
Wt. of first ppt	0.0369	0.1407	0.2102	0.2796	0.3490
Wt. of second ppt	0.0349	0.1395	0.2094	0.2793	0.3487

An inspection of these results confirms the conclusions of Richards that the amount of occlusion is proportional to the concentration of the non-dissociated magnesium oxalate in the solution. These results seem to show that by a careful adjustment of the amount of precipitant to the amount of both calcium and magnesium present a satisfactory separation can be effected by a single precipitation in all cases except those in which the amount of magnesium is very large as compared to the amount of calcium.

In the last series of experiments which are reported below, the method was further modified by making the precipitation in two stages: in the first stage sufficient oxalic acid to combine with all the calcium was added, then slowly neutralized with ammonium hydroxide and allowed to stand for ten minutes; in the second stage the balance of the oxalic acid was added, the solution made alkaline and allowed to stand for an hour.

No. of experiment.	XV.	XVI.	XVII.	XVIII.	XIX.
Wt. of CaO added	0.0350	0.1400	0.2100	0.2800	0.3500
Wt. of MgO used	0.3500	0.2800	0.2100	0.1400	0.0350
Wt. of $(COOH)_22H_2O$	1.000	1.000	1.000	1.000	1.000
Wt. of first ppt	0.0362	0.1404	0.2099	0.2798	0.3495
Wt. of second ppt	0.0352	0.1397	0.2094	0.2794	0.3491

These results show a decided improvement over the previous series and indicate the fact that very little occlusion takes place under these conditions of precipitation, that is so long as there is sufficient calcium to take up the C_2O_4 ions present. This method of making the separation may then be depended upon except in those cases in which the amount of magnesium present is ten times as great as the calcium.

Conclusions.—In the determination of calcium in mixtures of calcium and magnesium carbonates no difficulty is experienced in obtaining a good separation of the calcium by a single precipitation if 0.6 g. of the sample is employed, if the solution contains 3.5 g. of ammonium chloride and is diluted to 300 cc. and heated to boiling before precipitation, if precipitation is effected by the addition of 1 g. of oxalic acid and neutralization, during an interval of five minutes, with a one per cent. solution of ammonium hydroxide, and if the precipitate is allowed to stand for an hour, provided the amount of magnesium present does not greatly exceed the amount of calcium. If the relative amount of magnesium present is still greater this method should be further modified by effecting precipitation in two stages, during the first of which only sufficient precipitant to combine with all the calcium present is added. If the amount of magnesium is ten times as great as the calcium it is difficult to obtain a perfect separation by a single precipitation.

Finally it may be noted that the coarsely crystalline character of the precipitate which is obtained when the calcium oxalate is separated from an acid solution is in itself a sufficient object to justify the exclusive use of this method of making the precipitation.

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A STUDY OF THE PHENOLSULPHONIC ACID METHOD FOR THE DETERMINATION OF NITRATES IN WATER.

I. THE COMPOSITION OF THE REAGENT AND OF THE REACTION PRODUCT.

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Received June 11, 1909.

The use of phenolsulphonic acid for the detection and determination of nitrates was first proposed by Sprengel (1) in 1863, and attention was called to this suggestion by Kekulé (3, 6) in 1867, who incorporated the method in his *Lehrbuch*, but it was not until 1885 that the process was placed upon a practical basis by Grandval and Lajoux (2) and described by them in substantially the same form in which it is used today. Briefly this consists in pouring over the dry nitrate-containing material a few cubic centimeters of a mixture of phenol dissolved in concentrated sulphuric acid. After standing a few moments, water is added and the mixture made alkaline with ammonium hydroxide or sodium or potassium hydroxide. The yellow color resulting is then matched in a colorimeter with a similarly treated known amount of nitrate.

Grandval and Lajoux believed that their reagent contained a mono-