[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE OXALATE METHOD FOR SEPARATING CALCIUM AND MAGNESIUM

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The use of the oxalate anion for the quantitative precipitation of calcium in the presence of magnesium cations probably dates from Bergmann, the father of analytical chemistry, for it is mentioned in a Latin paper covering the work of Bergmann, which was published in 1778. Bucholz in a paper written in 1812 casually mentions the reaction as if it were well known to chemists at that time.

C. R. Fresenius, in his classic text on analytical chemistry, recommended, at about 1850, a dilute solution, the presence of sufficient ammonium chloride to prevent the precipitation of magnesium hydroxide and sufficient ammonium oxalate to combine with both calcium and magnesium. Fresenius stated that more oxalate than that required by the calcium is necessary because magnesium tends to prevent the precipitation of calcium oxalate. He recommended that the precipitate be allowed to stand twelve hours to insure complete precipitation of the calcium and that the precipitate be dissolved in hydrochloric acid and again treated with ammonia and oxalate in order to obtain a pure precipitate free from magnesium.

Down to the beginning of the nineteenth century, the statements of Fresenius regarding the oxalate precipitation of calcium were for the most part regarded as authoritative, although a number of chemists criticized the method, notably Sherer, who in 1858 preferred to separate calcium and magnesium ions by means of dilute sulfuric acid and considerable alcohol.

In 1901, Richards, McCaffrey and Bisbee[1] studied the ammonium oxalate separation from the standpoint of the physical chemist, and succeeded in avoiding the double precipitation. According to Richards, the hot, slightly acid solution of calcium and magnesium chlorides is first treated with an excess of oxalic acid and is then neutralized slowly during about fifteen minutes. Then the solution is made distinctly ammoniacal and a *large excess* of ammonium oxalate is added.

A careful study of Richards' paper fails to show exactly what is meant by a "large excess of ammonium oxalate" and the reason for the excess appears to be the idea of making the calcium oxalate less soluble in accordance with the solubility product principle and the common ion effect.

Blasdale[2] subsequently modified the procedure of Richards and obtained good results with much less oxalate. For a solution containing the equiv-

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[1] Richards, McCaffrey and Bisbee, *Proc. Am. Acad. Arts Sci.*, **36**, 375 (1901); *Z. anorg. Chem.*, **28**, 71 (1901).

[2] Blasdale, THIS JOURNAL, **31**, 917 (1909).

alent of not more than 0.6 g. of the mixed oxides in a volume of 300 cc. Blasdale recommended adding to the boiling solution 3.5 g. of ammonium chloride and only one gram of oxalic acid. If the content of magnesium is very high, only enough oxalate to precipitate the calcium is added at the start and the rest only after the solution has been slowly neutralized and allowed to stand for ten minutes. A double precipitation is advised when ten times as much magnesium as calcium is present and when the content of ammonium salts is high it is advised to remove them before precipitating the magnesium.

Dede[3] determined the calcium content of burnt magnesia and held that the addition of 2 g. of ammonium oxalate was necessary. Luff[4] avoided the use of excess ammonium oxalate and Bach[5] states that a bad separation of a little calcium from considerable magnesium always results if the ammonium chloride content is low or the ammonium oxalate content is high.

Recently two very contradictory papers have been written on the separation of small quantities of calcium from considerable magnesium. Hahn and Weiler[6] claim that a good separation is obtained when only a *slight excess* of ammonium oxalate is used while Bobtelsky and Frau Malkowa-Janowskaja[7] obtained excellent results by adding 20 g. of ammonium oxalate to 100 cc. of hot solution containing calcium and magnesium. In this way, prompt precipitation of 20 mg. of calcium was obtained in the presence of 2.70 g. of magnesium chloride.

The above citations represent but a very small part of the voluminous literature on the separation of calcium and magnesium. It is clear that chemists differ widely with respect to how much ammonium oxalate should be used to accomplish the best results. In order to settle this matter in our own minds, we have made quite a number of experiments, the enumeration of which would be very boring but the results seem quite clear.

The statement by Fresenius that more oxalate is required when magnesium is present than would be necessary in a solution of pure calcium chloride is true. Thus, with a sample of pure calcium carbonate weighing 0.5 g. (10 milliequivalents), correct results were obtained by using 50 cc. of 0.5 N ammonium oxalate solution as precipitant. When, however, 0.5 g. of calcium carbonate was present together with 0.5 g. of basic magnesium oxalate, only 4.06 and 4.12% of calcium were obtained when 7.40% of calcium was present by using 5 cc. of the reagent. In fact, with only 0.05 g. of calcium carbonate in the mixture, the results were low with 50 cc. of reagent. Correct results were obtained when one milliequivalent of cal-

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[3] Dede, *Chem.-Ztg.*, **36**, 414 (1909).

[4] Luff, *Z. anal. Chem.*, **65**, 439–448 (1925).

[5] Bach, *Chem.-Ztg.*, **49**, 514 (1925).

[6] Hahn and Weiler, *Z. anal. Chem.*, **70**, 1–22 (1926).

[7] Bobtelsky and Malkowa-Janowskaja, *Z. angew. Chem.*, **40**, 1434–1437 (1927).

cium was present together with five milliequivalents of magnesium only by adding 35 milliequivalents of oxalate. In every case the precipitate was allowed to stand overnight before filtering.

Fresenius' statement that magnesium oxalate is likely to be formed if considerable ammonium oxalate is added, does not appear to be true when the solution is fairly dilute and the precipitation is accomplished as recommended by Richards or by Blasdale. With a sample weighing 0.5 g. and containing 24.5% of magnesium, the magnesium results were high when the precipitation of calcium was incomplete but were correct when 25–125 milliequivalents of ammonium oxalate was added to precipitate one milliequivalent of calcium.[8] The method of Bobtelsky and Frau Malkowa-Janowskaja is based on some solubility studies which show that ammonium chloride solutions dissolve more magnesium oxalate than pure water does and that the solvent effect of ammonium oxalate on magnesium oxalate is much more marked. A number of experiments were made[9] using 20 grams of ammonium oxalate to precipitate a small quantity of calcium in the presence of considerable magnesium. The results obtained were in close agreement with those obtained by the method of Richards or by a double precipitation of calcium. The statement that there is no precipitation of magnesium when this very large excess of oxalate is used to precipitate a little calcium appears to be correct.

The presence of this large excess of ammonium oxalate has, however, a decidedly unfavorable effect upon the subsequent determination of magnesium. In the first experiment by Mr. Gardner in which 20 g. of ammonium oxalate was used, there was absolutely no precipitation of magnesium ammonium phosphate by the method of Smitz, although the solution was allowed to stand for several days. In another experiment a solution was used from which 0.1775 g. of magnesium pyrophosphate should have been obtained, as it was when only 5 g. of ammonium oxalate was used. This solution, when 20 g. of ammonium oxalate was present, yielded only 0.0154 g. of magnesium pyrophosphate by the Smitz method but after evaporating the filtrate to dryness, expelling ammonium salts and taking up in dilute acid, an additional 0.1618 g. of magnesium pyrophosphate was obtained on repeating the precipitation.

Recently it has been recommended to determine magnesium by precipitation with *o*-hydroxyquinoline.[10] This precipitant gives a crystalline precipitate, easy to handle, in solutions which are slightly alkaline. Our

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[8] These conclusions are based on the results of twenty-two experiments by Arnold A. Smith. The experiments were carried out in duplicate and consistent values obtained with each duplicate.

[9] Experiments of Howard S. Gardner.

[10] R. Berg, *J. prakt. Chem.*, **115**, 18, 178–185 (1927); Hahn and Vieweg, *Z. anal. Chem.*, **71**, 122–130 (1927).

experiments[11] show, however, that the presence of a large excess of ammonium oxalate prevents the complete precipitation of this organic salt of magnesium. All the results were too low when much oxalate was present.

Neubauer,[12] Gooch and Austin,[13] Järvinen,[14] and Smitz have all found that the precipitation of magnesium succeeds in the presence of considerable ammonium salt, but it is evident that they never tried the experiment with as much ammonium oxalate present as recommended by Bobtelsky. In giving beginners a sample of dolomite to analyze for calcium and magnesium, the results obtained are usually good when the directions of Richards or of Blasdale are followed and a single precipitation of calcium oxalate made, or when, according to the directions of Fresenius,[15] a double precipitation of calcium oxalate is made. Occasionally, however, we have noticed that a student fails to get all of the magnesium precipitated as magnesium ammonium phosphate. In the light of these experiments it seems probable that this is the result of using too large an excess of ammonium oxalate. These experiments indicate that 75 cc. of 0.5 *N* ammonium oxalate solution is sufficient for the precipitation of 0.3 g. of calcium ions in a volume of 500 cc., but the same quantity of reagent should be used when only 0.02 g. of calcium is present in the presence of considerable magnesium (0.12 g.).

Summary

For the precipitation of calcium oxalate in the presence of magnesium ions an excess of ammonium oxalate is necessary. If this excess is properly regulated, it is possible to precipitate pure calcium oxalate. If, however, a very large quantity of ammonium oxalate is present, the precipitation of magnesium ammonium phosphate is incomplete even after long standing.

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NOTE

The Rate of Reaction of Liquid and Gaseous Zinc with Carbon Monoxide.[1]—The data of Maier and Ralston[2] on the free energy of zinc oxide and Lewis and Randall's[3] equation for the free energy of carbon monoxide indicate that at all except extremely small partial pressures,

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[11] Performed by Mr. Waite.

[12] Neubauer, *Z. angew. Chem.*, **9**, 435 (1896).

[13] Gooch and Austin, *Am. J. Sci.*, [4] **7**, 187 (1899).

[14] Järvinen, *Z. anal. Chem.*, **44**, 333 (1905).

[15] Cf. Hillebrand, "Analysis of Silicate and Carbonate Rocks."

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[2] Maier and Ralston, THIS JOURNAL, **38**, 364 (1926).

[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 576.