

A MODIFICATION OF THE PROCEDURE FOR THE QUALITATIVE SEPARATION OF THE METALS OF THE ALKALINE-EARTH GROUP.—BY C. B. NICKERSON, M. A., Professor of Chemistry, Dalhousie University.

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The separation of the ions, Barium-Strontium-Calcium, has always furnished something of a problem to teachers of Qualitative Analysis. Although several very excellent methods of analysis are available, the writer has found them to be somewhat tedious of manipulation, and requiring more time for a successful separation than is usually convenient for the ordinary college class in Qualitative Analysis. It is not the purpose of this paper to go into the various reasons why the separation of these ions is a difficult one, but rather to describe a method which has been used successfully by the writer in his classes for a number of years.

This method depends upon the separation of calcium from strontium by taking advantage of the solubility of calcium sulphate in a boiling solution containing a considerable quantity of ammonium acetate. The solubility of calcium sulphate, and the insolubility of strontium sulphate in solutions of ammonium sulphate and ammonium chloride have been known for a long time and several procedures for the qualitative separation of these ions are based on this principle. The substitution of ammonium acetate for the chloride or sulphate however, has been found to be generally more suitable and also, in the hands of students, capable of greater accuracy. The separation of barium ion from calcium and strontium ions by the well known acetic acid-chromate method has also been studied quantitatively, and a modification of the usual method of separation proposed.

Procedure.

Treatment of the Filtrate from the Sulphides of the Fe.-Zn. etc. group.

Boil the solution until free from H_2S . Filter if necessary and add NH_4Cl , (if it has not already been added). Make ammoniacal and add 10-20 cc of ammonium carbonate solution. (The temperature of the solution at the time of the addition of ammonium carbonate should not exceed $70^\circ C.$)* Filter and test for completeness of precipitation. The precipitate may now contain the carbonates of barium, strontium and calcium; the filtrate will contain the ions of the alkali group with magnesium ion.

Treatment of the Precipitate.

Dissolve the precipitate by pouring over it 10 cc of 3 N. acetic acid. Continue this treatment, using the same 10 cc of acid, until all action is over. Carefully neutralize the acetic acid solution with ammonium hydroxide and then add 3 cc of acetic acid in excess. Next add about 10-15 cc of potassium chromate solution: a yellow precipitate is barium chromate and confirms the presence of barium. Heat to boiling, let stand 10 minutes, and filter. To the clear filtrate, which should be orange yellow in color with the excess of di-chromate ions, add 10 cc of acetic acid, a strong excess of ammonium hydroxide, and 10 cc of ammonium sulphate solution. (The solution should have a volume of approximately 100 cc at this point.) Boil for about two minutes; a white precipitate is strontium sulphate and confirms the presence of strontium. Let stand for about ten minutes and filter.

To the clear filtrate add 10 cc of ammonium oxalate solution. If no precipitation occurs at once, boil for a few moments; a white precipitate is calcium oxalate and confirms the presence of calcium.

The usual and most satisfactory method of studying problems of this kind is to determine the analytical limits involved. That is, to find the minimum quantity of one ion which can be detected in presence of a maximum quantity of the other. With this idea in view solutions were prepared of the following

*H. B. Vickery: these Transactions, Vol. XIV, page 31.

concentrations. The ordinary C. P. chemicals were used in all cases.

Acetic Acid.....	3 N. solution
Ammonium Hydroxide.....	3 N. solution.
Ammonium Carbonate.....	3 N. solution.
Ammonium Sulphate.....	10% solution.
Ammonium Oxalate.....	Saturated solution at 15° C.
Potassium Chromate.....	10% solution.

Test solutions of the chlorides of barium, strontium and calcium were prepared of such concentration that 1 cc of solution contained 5 mgs. of the metal.

Separation of Ba and Sr.

The method given in the procedure above for the separation of these ions involves nothing new. It was necessary however to study the separation quantitatively to determine its practical limits of accuracy so far as this particular procedure was concerned. Assuming that the detection of about 2 mgs. of barium in 100 cc's of solution represents reasonable accuracy in a separation of this kind, it was only necessary to determine the amount of acetic acid which would allow the precipitation of that quantity of barium as barium chromate, and also to determine the maximum amount of strontium chromate which could be held in solution by the same concentration of acetic acid.

Separation of Barium and Strontium.

Separations of barium and strontium were carried out according to the method given, using varying concentrations of acetic acid. The solubility of the barium chromate was found to increase rapidly as the excess of acetic acid was increased. With an excess of 3 cc's of 3 N. acetic acid, it was found that 1.5 mgs. of barium gave a noticeable precipitate of barium chromate, while under similar conditions, as much as 500 mgs. of strontium gave no trace of precipitate.

The usual source of error at this point is of course, that when barium is present alone and in considerable quantity, there may not be sufficient quantity of acetic acid present to hold all of it in solution as the chromate, and as a result, some of the barium may be precipitated in place of strontium as the sulphate. Tests were made, therefore, to determine the maximum amounts of barium which could be present under the conditions of the procedure. It was found that a solution containing 400 mgs. of barium and no strontium, failed to give the slightest precipitate as the sulphate after having been removed as the chromate in presence of 3 cc's of acid.

Separation of Strontium and Calcium

The problem to be studied in this separation was the extent to which calcium sulphate is dissolved by ammonium acetate under the conditions of experiment, and also to find the minimum quantity of strontium that could be detected by precipitation as the sulphate. In an investigation of this separation using ammonium sulphate and ammonium chloride, Vickery* has found that 80 cc's of a 10% solution of ammonium chloride were necessary to prevent all precipitation of calcium sulphate in a solution containing 200 mgs. of calcium, and that under similar conditions, 3 mgs. of strontium gave a faint turbidity.

Solutions were prepared containing varying quantities of strontium and calcium, and separations were carried out according to the procedure given. It was found that 3 mgs. of strontium could readily be detected in the presence of 400 mgs. of calcium. Also it was found that a solution containing only 400 mgs. of strontium gave not the slightest test for calcium.

It is apparent therefore, that the substitution of ammonium acetate for the chloride or sulphate offers a wider limit for the delicacy of the strontium-calcium separation. The final detection of calcium in the filtrate from strontium sulphate depends upon the well known oxalate precipitation, and of course,

*These Transactions, Vol. XIV, page 30.

needs no further verification. No confirmatory tests for the three ions have been included in the procedure given. It is assumed however that the usual ones are to be applied whenever it is thought necessary.

No claims are made for exceptional accuracy in the above mentioned procedure. It is not intended to replace the various methods which are in general use by experienced analysts. In the writer's opinion, it does, within reasonable limits, offer an accurate method of analysis for a rather troublesome group of metals.