

AN INVESTIGATION OF THE "CHROMATE METHOD" FOR  
SEPARATING THE ALKALINE EARTHS.\*—BY HUBERT  
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This investigation was undertaken with the twofold object of discovering the degree of sensitiveness of which the ordinary "chromate method" for the separation of the alkaline earths is capable, and also under what conditions this sensitiveness may be increased. Incidentally a considerable improvement was made in the procedure.

Throughout the experimental work the idea was kept constantly in mind to have the conditions of working as nearly as possible those which obtain in the manipulation of the average student of qualitative analysis, and where these have been changed, to make them very easily attainable, so that the final quantitative results might fairly represent the degree of accuracy obtainable in ordinary work.

While several methods exist for the separation of the alkaline earths which are extremely delicate, † they depend largely upon the use of alcohol and ether to decrease the solubility of the various precipitates, and hence are scarcely suitable for class use. The chromate method, on the contrary, uses water solutions alone and obviates the necessity for inconveniently long waits for complete precipitations, thus greatly decreasing the time required for a single analysis and making this method eminently suitable for use in class. The procedure ordinarily followed ‡ consisted in precipitating the carbonate in strongly alkaline solution, magnesium being held in solution by means of ammonium chloride. The

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\* Contributions from the Science Laboratories of Dalhousie University (Chemistry).

† J. Am. Chem. Soc., **30**, 611. (1909).

‡ G. S. Newth: Manual of Chemical Analysis, p. 35.

carbonates were then dissolved in the least possible quantity of acetic acid, the solution diluted, barium removed as chromate, and ammonium sulphate added to the filtrate. This was supposed to throw down the insoluble strontium sulphate, but retain the calcium by its solvent action upon calcium sulphate.

It was at this point that difficulty was usually encountered as the calcium almost invariably came down in some quantity, especially if present in large amounts, rendering a complete separation impossible and obscuring the confirmatory flame tests. However, sufficient calcium was retained to give the confirmatory oxalate test, and by again bringing the precipitate into solution and treating with a solution of calcium sulphate, the strontium was confirmed even in the presence of a large amount of calcium. This method, resulting as it does in only an approximate separation, is unsatisfactory, and attempts were made to improve it.

Solutions of barium, strontium and calcium as chlorides were made up and carefully standardized gravimetrically, the first two by precipitating a known volume with silver nitrate, and the last with ammonium oxalate. Appropriate volumes of these solutions were run from burettes into flasks and made up so that each solution should contain a milligram of the metal per cubic centimeter. These standard solutions were used for the analysis.

The first step was to investigate quantitatively each precipitation occurring throughout the procedure and record its delicacy under the conditions normally occurring in the course of an analysis. The method followed was to run various quantities of the standard solutions into a series of beakers, dilute them with hot water, and add the cold reagents in the order given. This resulted in the precipitation taking place at a temperature of 65°-70°. By watching the row of beakers it was easy to compare the amounts of precipitate occurring and to find that one which yielded no precipitate,

thus fixing a lower limit to the sensitiveness of the particular precipitation, and ensuring uniform conditions.

The reagents used were:—Ammonia sp. gr. .90 (equivalent to three times the volume of sp. gr. .96).

Ammonium Chloride.....	10%
Ammonium Carbonate.....	25%
Potassium Chromate.....	5%
Ammonium Sulphate.....	10%
Ammonium Oxalate.....	5%
Acetic Acid.....	50%

#### BARIUM CARBONATE

The precipitating reagents were 3cc  $\text{NH}_4\text{OH}$ , 10cc  $\text{NH}_4\text{Cl}$ , 10cc  $(\text{NH}_4)_2\text{CO}_3$ . The total volume of the solution was 100cc.

- 0.5 mg. of barium gave no precipitate.
- 1.0 mg. gave no precipitate.
- 2.0 mg. gave no precipitate.
- 3.00 mg. gave very slight deposit on lines of rubbing with glass rod.
- 5.0 mg. gave slight deposit.
- 7.0 mg. gave very slight precipitate.
- 10.0 mg. gave feathery crystalline precipitate in few moments.
- 25.0 mg. gave feathery precipitate almost at once.

#### STRONTIUM CARBONATE

Conditions same as above.

- 0.5 mg. of strontium gave no precipitate.
- 1.0 mg. gave very slight precipitate in 5 minutes.
- 2.0 mg. gave slight precipitate in four minutes.
- 4.0 mg. gave decided precipitate in few moments.
- 10.0 mg. gave fairly heavy precipitate, but not coming down instantly.
- 25.0 mg. gave heavy precipitate at once.

## CALCIUM CARBONATE

Conditions same as above.

0.3 mg. of calcium gave no precipitate.

0.5 mg. gave no precipitate.

0.6 mg. gave very slight precipitate.

0.8 mg. gave slight precipitate.

1.0 mg. gave slight precipitate in 4 minutes.

5.0 mg. gave precipitate almost at once.

10.0 mg. gave heavy crystalline precipitate at once.

It was found that a temperature much in excess of 70° caused an interaction of the carbonate with the ammonium chloride, giving an evolution of carbon dioxide and resulting in the solution of the precipitate or complete failure to form a precipitate.

In each case completeness of precipitation of a solution containing 25 mg. of the metal was tested by filtering after ten minutes and allowing to stand over night. Only in the case of barium did any deposit form and even in this case it was in very small quantity. The precipitates were examined microscopically, but it was found that although the crystals when falling from very dilute solutions were quite easily differentiated, from more concentrated solutions they were almost indistinguishable, especially since calcium, and to a lesser extent barium, show a tendency to come down as gelatinous masses from cool solutions.

## BARIUM CHROMATE

Precipitating reagent, 3cc  $K_2CrO_4$ . Total volume of solution, 100cc.

In neutral solution, even one tenth of a milligram of barium gave a cloudiness in five minutes, but in a solution containing 1-2cc acetic acid 2 mg. failed to give a precipitate, while 2.5 mg. gave a slight one on standing a few

minutes. 5 mg. gave a precipitate almost at once. Boiling temperature was used.

#### STRONTIUM CHROMATE

Precipitating reagent, 15cc  $K_2CrO_4$ . Total volume of solution, 200cc.

In neutral solution 200 mg. of strontium gave a very slight deposit in beaker in ten minutes. 400 mg. gave a heavy precipitate in a few moments. In solution containing acetic acid, 500 mg. failed to give a precipitate over night.

#### CALCIUM CHROMATE

Conditions same as in precipitation of strontium chromate.

In neutral solution 500 mg. of calcium gave a barely perceptible precipitate in fifteen minutes, while in acid solution none formed at all.

The barium chromate when suddenly thrown down is very fine and scarcely crystalline, but boiling for a few minutes causes it to crystallize. Under the conditions of ordinary work there is little risk of obtaining a precipitate of strontium chromate, while the barium is almost completely removed.

#### STRONTIUM SULPHATE

Precipitating reagent, 10cc  $(NH_4)_2SO_4$ .

2 mg. failed to give a precipitate on boiling while 2.5 mg. gave a scarcely perceptible one. 4 mg. gave very slight precipitate on standing. 10mg. gave a precipitate in a few moments. The experiments were repeated with both neutral and acetic acid solutions, with practically identical results.

#### CALCIUM SULPHATE

Precipitating reagents, 2cc acetic acid, 10cc  $(NH_4)_2SO_4$ . Temperature, 70°C.

200 mg. gave heavy feathery precipitate at once.

100 mg. gave small precipitate in one minute, which rapidly increased in size.

90 mg. gave small precipitate on standing an hour.

75 mg. gave no precipitate on standing.

Thus, under the conditions of ordinary work, calcium when present in excess of 90 mg. is precipitated along with the strontium. 200 mg. of calcium, and 40cc of  $(\text{NH}_4)_2\text{SO}_4$  gave a heavy precipitate on warming, but no solvent action was noticeable on boiling; 40cc more were added and boiled and a slight solvent action took place. On adding 40cc of ammonium chloride to this solution it was observed that the greater part of the precipitate went into solution on boiling for a few moments. As this action appeared important, it was determined to investigate it further.

To try the effect of the addition of ammonium chloride before precipitating the sulphate, two solutions of 400 mg. of calcium each were prepared. To No. 1 were added 40cc  $\text{NH}_4\text{Cl}$  and to each 1cc of acetic acid. Both were brought to  $70^\circ$  and 10cc  $(\text{NH}_4)_2\text{SO}_4$  added. The effect of the ammonium chloride was very noticeable, for in five minutes only a very few crystals had appeared in No. 1, and very little deposit had formed on the bottom of the beaker, while in the second beaker the precipitation had been heavy and was nearly complete. Other experiments were tried, and it was found that 80cc of ammonium chloride solution were sufficient to prevent completely the precipitation of 200 mg. of calcium, while 50cc failed to do so, as a slight deposit formed on boiling. 160cc were sufficient to hold up 400 mg. of calcium, showing that there should be 80cc of ammonium chloride present for each 200 mg. of calcium. It was found that the total volume should be not less than 150cc as a smaller volume rendered the precipitation of the calcium more likely. The effect of the ammonium chloride upon the strontium was investigated, and it was found that in the presence of a large excess, 4 mg. gave a precipitate on boiling, while 3mg. gave a very slight turbidity. Thus the effect is scarcely appreciable. The amount

of ammonium chloride is perhaps somewhat excessive, but it was found that when much smaller quantities were used, the calcium was liable to fall when the solution was boiled or digested on the water-bath. It is quite easy to tell from the character of the precipitate at this point if the calcium is precipitating. The strontium precipitate is very fine grained and falls immediately. The calcium sulphate precipitate, especially if ammonium chloride is present, is feathery, crystalline and forms slowly. It usually forms first at the surface, and is particularly liable to come down on boiling.

#### CALCIUM OXALATE

0.1 mg. of calcium gave a perceptible precipitate on standing for a few minutes. The effect of ammonium chloride in considerable quantities seemed to be to make the precipitation rather slower, but 0.1 mg. could still be easily detected.

#### SENSITIVENESS OF METHOD

The next step in the investigation was to carry out a series of analyses under normal conditions, using large excess of two of the metals and varying small quantities of the third until it could no longer be detected by the methods used. In this way the limit of detectability for each metal in the presence of excess of the others was found *when the complete analysis is carried through.*

A solution containing 4 mg. of barium and 200 mg. each of calcium and strontium was made up. The carbonates were precipitated and allowed to digest at 70° for 15 minutes, and then filtered and dissolved as usual. A slight precipitate formed in 5 minutes after adding 5cc of the chromate and on boiling and filtering a distinct yellow deposit was left on the filter after washing the potassium chromate out. A similar solution, but containing only 3 mg. of barium

as chloride, failed to form a precipitate in 15 minutes, or to leave a deposit on the filter. Hence the limit of detection of barium using the ordinary procedure is 4 mg. when excess of the others is present.

A solution containing 15 mg. of strontium and 200 mg. each of calcium and barium was treated by the ordinary procedure and the barium removed. Insufficient ammonium chloride was added and a considerable precipitate formed with the ammonium sulphate. This was boiled with ammonium carbonate and dissolved in acetic acid and calcium sulphate added. A very fine precipitate formed in the course of a few hours. A similar solution was taken and sufficient ammonium chloride (i.e. 80cc) was added, after removing the barium, to hold up the calcium. A very fine granular precipitate was obtained with ammonium sulphate in a few minutes, and no trace of the typical calcium crystals. Its identity was easily established. A solution with 13 mg. of strontium failed to give a precipitate, hence the limit of detectability of strontium is 15 mg. when an excess of barium and calcium is present.

A solution containing 1 mg. of calcium, 200 mg. of barium and 500 mg. of strontium was treated as before, and the barium and strontium removed as chromate and sulphate respectively. A fine white precipitate appeared in a few moments on making alkaline and adding ammonium oxalate. A solution containing 0.5 mg. gave no precipitate on boiling 15 minutes, but gave a very fine deposit on standing overnight. Hence, the limit of detectability of calcium is 1 mg. or somewhat under, when excess of barium and strontium are present.

#### PROPOSED PROCEDURE

The results of the investigation can best be summarized by giving a procedure with notes for the separation of the alkaline earths by the improved chromate process.



PROCEDURE I. *Precipitation of group (after ridding of sulphur).*

To solution after removal of iron and zinc group, (60cc), add 10cc  $\text{NH}_4\text{OH}$ , 20cc  $\text{NH}_4\text{Cl}$  and 20cc  $(\text{NH}_4)_2\text{CO}_3$  at a temperature of  $70^\circ$ , and let stand several minutes. Filter and wash with little cold water.

*Notes*—1. At temperature much above  $70^\circ$  the carbonates react with the ammonium chloride forming the soluble chloride with evolution of carbon dioxide.

2. At temperature much lower calcium comes down as a gelatinous mass and barium also has this tendency. Warming on the water bath will cause them to crystallize.

3. Precipitation of strontium and calcium is complete in 10 minutes and of barium very nearly so.

PROCEDURE II. *Precipitation of Barium.*

Pour a 5cc portion of acetic acid through the filter a few drops at a time, and pour through repeatedly until it runs through clear. Then wash thoroughly with hot water. Make up to 80cc and heat to boiling. Add 5cc of  $\text{K}_2\text{CrO}_4$  solution a few drops at a time with constant stirring and boil a few moments. Filter and wash with cold water. (Yellow precipitate shows presence of barium)

*Notes*—1. The 5cc of 50% acid should be diluted somewhat and used hot.

2. 500 mg. of calcium and strontium fail to precipitate under these conditions while 4 mg. of barium give a distinct test.

3. The filtrate should be yellow rather than red, but should be tested with another drop of chromate.

PROCEDURE III. *Confirmatory test for Barium.*

Pour a little hot  $\text{HCl}$  through the filter repeatedly and evaporate almost to dryness. Test in flame on platinum wire. Green color confirms barium.

PROCEDURE IV. *Precipitation of Strontium*

Evaporate to about 80cc and add 80cc of  $\text{NH}_4\text{Cl}$  for every 200 mg. of barium present; in no case less than 80cc. Add 10-15cc  $(\text{NH}_4)_2\text{SO}_4$  solution. *Fine granular white precipitate* indicates strontium. Heat to boiling and let digest a few moments. Filter and wash with hot water.

*Notes*—1. Calcium, if present to the extent of 100 mg., will precipitate at this point unless held in solution by a large quantity of  $\text{NH}_4\text{Cl}$ . If a feathery precipitate in quite large crystals appears on heating, it is probably calcium.

2. Ammonium chloride inhibits the precipitate of strontium to only a very slight extent.

3. 15 mg. of strontium can be easily detected in the presence of large amounts of barium.

3. The confirmatory test should always be tried.

PROCEDURE V. *Confirmatory test for Strontium.*

Boil the precipitated sulphate with ammonium carbonate and neutralize with acetic acid. Concentrate to 10-20cc and filter if necessary. Add saturated solution of  $\text{CaSO}_4$  and boil. Fine white precipitate confirms strontium.

*Note*—1. The strontium sulphate is converted to carbonate by the ammonium carbonate and brought into solution by the acid. The calcium is likewise converted but calcium acetate cannot give a precipitate with calcium sulphate, while the less soluble strontium sulphate separates at once on heating.

PROCEDURE VI. *Precipitation of Calcium.*

To the hot filtrate add  $\text{NH}_4\text{OH}$  to strongly alkaline reaction and then 10cc more. Add 20cc hot  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution and stir. White precipitate indicates barium.

*Note*—1. 1 mg. of calcium can be easily detected in the presence of 400 mg. of barium and strontium.

SUMMARY

1. Each precipitation occurring in the chromate process for the separation of the alkaline earths has been quantitatively investigated.

2. The chromate process has been found not to effect an exact separation of the three metals.

3. An improvement has been suggested by which the separation is practically complete, and a procedure formulated.

4. The limit of detectability for each metal by this procedure has been determined.