

A PROCEDURE FOR THE QUALITATIVE ANALYSIS OF THE GROUP:
MAGNESIUM, POTASSIUM, SODIUM.—BY HAROLD S. KING,
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The course of qualitative analysis as given at Dalhousie University is so arranged that magnesium is not precipitated with the alkaline earth group but is found associated with the alkali metal group. In this paper a procedure is outlined for the analysis of the last group in the basic analysis, i.e. magnesium, potassium and sodium.

The classical method of analyzing for these constituents is to test for magnesium by the phosphate method in a side sample and, if present, to evaporate the solution to dryness and ignite to remove ammonium salts. Then the magnesium is precipitated as hydroxide by means of barium hydroxide, the excess barium is removed as carbonate by the addition of ammonium hydroxide and ammonium carbonate. The solution is evaporated and ignited a second time to remove ammonium salts, and the residue is analyzed for potassium and sodium. The difficulties with this standard procedure are that the barium hydroxide solution absorbs carbon dioxide readily, the filtering and washing of the precipitates are slow, and particularly, two separate evaporations and ignitions are necessary.

The procedure about to be described is found to be somewhat simpler in operation. Its main features are made plain in the accompanying outline, while the detailed description and discussion of the procedure are as follows:

Procedure 1. Detection of Magnesium.

Evaporate the filtrate from the alkaline earth group precipitation until crystals appear. Add 15 c.c. of 15n. NH_4OH and 5-20 c.c. of 4n. H_3PO_4 . A white granular precipitate may be MgNH_4PO_4 and indicates the presence of magnesium. Filter and wash once. Treat the precipitate by P.2 and the filtrate by P.3.

NOTES.—1. Because of the reaction $\text{MgNH}_4\text{PO}_4 + \text{H}_2\text{O} = \text{NH}_4\text{OH} + \text{MgHPO}_4$, a large excess of NH_4OH is used.

2. Only the minimum quantity of H_3PO_4 necessary should be added. Too large an excess causes the solution used in P.7 to be too acid. The excess of phosphate may be removed before carrying out P.4 by adding hydrated ferric oxide and filtering.

3. If, at the beginning of the analysis of the iron and aluminium groups, phosphates were found to be present in the sample under investigation, it might be well at that point to add sufficient phosphoric acid to insure the complete precipitation of the alkaline earth group and magnesium as phosphates, and then to follow the procedure as given by C. B. Nickerson in his paper "Arrangement of Procedure for the Removal of Phosphate Ions from the Iron and Alkaline Earth Groups" published in the Transactions of the Nova Scotian Institute of Science, Vol. XIII, Part 2, pp. 95-98.

Procedure 2. Removal of Alkaline Earths.

Extract the precipitate from P.1 with 5 c.c. of 3n. H_2SO_4 . To the extract add 10 c.c. of methylated spirits and shake for a few minutes. Filter, if necessary.

NOTES.—1. Traces of the alkaline earth group may have escaped precipitation as carbonates. If so, they would be precipitated in P.1 by the phosphate in the form of a flocculent, NOT GRANULAR, precipitate. Therefore, the confirmatory test for magnesium should be carried out if the precipitate formed in P.1 is scanty or flocculent.

2. The sulphates of the alkaline earth group are insoluble in an alcoholic solution, though calcium sulphate is appreciably soluble in aqueous solution. Methylated spirits are used rather than ethyl alcohol because of the regulations concerning the use of the latter.

Procedure 3. Confirmatory Test for Magnesium.

Add to the filtrate from P.2 5 c.c. of 15n. NH_4OH and 5 c.c. of 4n. H_3PO_4 . Let stand at least half an hour with frequent shaking. A white granular precipitate is MgNH_4PO_4 and confirms the presence of magnesium.

NOTES.—1. H_3PO_4 is used rather than Na_2HPO_4 because the precipitate formed in the former case is more distinctly crystalline.

Procedure 4. Removal of Ammonium Salts.

Evaporate the filtrate from P.3 in a beaker until crystals appear. Then transfer to an evaporating dish and evaporate

to dryness. Ignite the residue carefully with a free flame until no more white fumes come off. (Hood.) Do not heat to red heat. Be sure to heat the sides of the dish as well as the bottom. Cool and add 10 c.c. of water. Heat just to boiling and filter through a very small filter paper into a test-tube. Bubble through this solution a fine stream of the oxides of nitrogen made by warming 1 gram of starch with 4 c.c. of nitric acid (Sp. Gr. 1.33) in a 100 c.c. flask. Then boil the solution in the test tube. Divide the solution into one-fourth and three-fourth portions. Treat the one-fourth portion by P.5 and the three-fourth portion by P.7.

NOTES.—1. The bulk of the ammonium salts is removed by volatilization. Care must be taken, however, not to heat to incipient redness because at this temperature NaCl and especially KCl are volatile.

2. A residue so small as to be almost invisible may contain sufficient potassium or sodium to give tests. Therefore, the procedures 5 and 7 should not be omitted.

3. The reagents used throughout the analysis may have dissolved enough silicic acid from the glass to give a white residue of silica at this point. A brown residue may be due to organic matter derived from the filter paper or to impurities in the ammonia used. The excess of phosphoric acid gives a residue also.

4. The oxides of nitrogen formed by the action of starch on nitric acid of Sp. Gr. 1.33 are approximately a one to one mixture of NO and NO₂. They form nitrous acid in solution which reacts with the last traces of the ammonium salts to give nitrogen. It is important to remove ammonium salts completely because they interfere with the potassium test.

5. The ammonia free solution is divided into two portions and the potassium and sodium are tested for without separating them. For extreme accuracy they may be separated by the perchlorate method as given in the "Exact method of analysis of the alkali group," by A. A. Noyes, in his "Qualitative Chemical Analysis."

Procedure 5. Detection of Potassium.

Dilute the one-fourth portion from P.4 to 5 c.c. and add 5 c.c. of Na₃Co(NO₂) reagent. Let stand for at least 10 minutes if no immediate precipitate forms. A yellow precipitate may be K₂NaCo(NO₂)₆ and indicates the presence of potassium. Treat by P.6 without filtering.

NOTES.—1. The sodium cobaltinitrite reagent is made up 0.1 formal in $\text{Na}_3\text{Co}(\text{NO}_2)_6$, 3n. in NaNO_2 and 1n. in CH_3COOH .

2. As little as 0.1 mg. of potassium can be detected in the above portion after long standing even in the presence of a large excess of sodium.

3. Incomplete precipitation of magnesium does not interfere with this test. For example, as much as 100 mgs. of magnesium give no precipitate and do not interfere with the precipitation of the potassium.

4. Ammonium gives a precipitate of $(\text{NH}_4)_2\text{NaCo}(\text{NO}_2)_6$ which is almost as insoluble as the potassium precipitate and very similar to it. Therefore every precaution is taken to remove ammonium previous to this test. Moreover, if the precipitate formed is scanty, the confirmatory test should be made.

Procedure 6. Confirmatory Test for Potassium.

Boil the solution from P.5 for a minute. Then cool and add 3 c.c. of the $\text{Na}_3\text{Co}(\text{NO}_2)_6$ reagent. Let stand for ten minutes. A yellow precipitate is $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ and confirms the presence of potassium.

NOTES.—1. The cobaltinitrite reagent contains an excess of sodium nitrite and acetic acid. On boiling, any ammonium present is decomposed by the nitrous acid. The cobaltinitrite is decomposed also, so that after cooling more of the reagent is added.

2. This confirmatory test is more satisfactory than the flame test because the presence of sodium does not interfere.

Procedure 7. Detection of Sodium.

To the three-fourth portion from P.4 add 5 c.c. of the $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ reagent. Let stand at least one hour or better overnight. A white, crystalline precipitate adhering to the walls of the test-tube is $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ and shows the presence of sodium.

NOTES.—1. The dipotassium dihydrogen pyroantimonate reagent is 0.05 formal in $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$, 0. 1n. in KOH and saturated with $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$. It must be freshly made because of its instability.

2. When the portion analyzed is free from other substances, as little as 0.5 mg. of sodium can be detected with this reagent. With large amounts of potassium present, 8 mgs. of sodium may escape detection. Therefore, for more delicate work, potassium should be removed. Usually, however, this accuracy is sufficient.

3. Magnesium and the alkaline earths give a flocculent precipitate which, in small quantities, does not interfere with the test. The sodium precipitate adheres in part to the walls of the test-tube while the flocculent precipitate can be removed easily by decanting.

4. The sodium precipitate has a great tendency to form a supersaturated solution. Rubbing the inside of the test tube with a stirring rod aids the precipitation. Sodium should not be considered absent until the solution has stood at least an hour or better overnight. Very often the compound comes down in the form of a few crystals rather than as a precipitate.

5. The flame test is not to be depended upon for the detection of sodium because of its extreme delicacy. The amounts of sodium introduced from the utensils, filter paper and dust give enough sodium to color the flame but not sufficient to detect by the pyroantimonate test.

Outline for the Analysis of Magnesium, Potassium and Sodium.

Filtrate from the Alkaline Earth Group Precipitation. (P.1) Evaporate. Add NH_4OH and H_3PO_4 . Filter.			
White granular ppte. MgNH_4PO_4 (P.2) Extract with H_2SO_4 . Add alcohol. Filter.		Filtrate: (P.4) Evaporate to dryness. Ignite. Dissolve in H_2O . Bubble in NO and NO_2 . Boil.	
Ppte. Alkaline Earth Sulphates Reject.	Filtrate: (P.3) Add NH_4OH and H_3PO_4 White gran. ppte. MgNH_4PO_4 . $\therefore \text{Mg}^{++}$	1/4 Solution. (P.5) Add $\text{Na}_3\text{Co}(\text{NO}_2)_6$ Yellow ppte. $\text{K}_2\text{NaCo}(\text{NO}_2)_6$.	3/4 Solution. (P.7) Add $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ White cryst. ppte. $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$.
		(P.6) Boil. Add $\text{Na}_3\text{Co}(\text{NO}_2)_6$ Yellow ppte. $\text{K}_2\text{NaCo}(\text{NO}_2)_6$. $\therefore \text{K}^+$	$\therefore \text{Na}^+$