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THE SEPARATION OF MAGNESIUM FROM THE ALKALI METALS

BY CARL OTTO

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In the various schemes of qualitative analysis which have been published, magnesium is usually included in the alkali group. Sometimes it is removed by precipitation before the tests for sodium and potassium are made, but more often it is not.

The presence of the magnesium ion interferes with the potassium pyroantimoniate test for sodium by producing a flocculent precipitate which masks the formation of the crystalline precipitate given by sodium with the above reagent. When magnesium is not removed sodium is detected by the flame test. This test has the disadvantage of being too delicate. Judgment must be exercised to decide whether the yellow flame coloration which is obtained could have originated from unavoidable contamination during analysis or is sufficient to indicate sodium in the original.

A simple separation of magnesium from the alkali metals (which does not seem to be used by anyone, for no reference can be found to it in the literature or in textbooks) is effected by the ignition of the nitrates of these metals. By acidifying the filtrate from the alkaline earth group with nitric acid and evaporating to dryness and again evaporating with nitric acid, almost all of the other anions which are present will be expelled. Ignition of the residue until ammonium salts and nitrogen oxides are entirely expelled converts the magnesium nitrate completely to magnesium oxide and the alkali nitrates partially to nitrites. The separation of these compounds can then be made by a few minutes' treatment with cold, dil. ammonium hydroxide. The alkali nitrites and nitrates are dissolved; the magnesium oxide remains undissolved, being less soluble in ammonium hydroxide than in water. It can then be dissolved in an acid and confirmed in the usual way, that is, with sodium phosphate in ammoniacal solution.

The advantage of this method of separation is an increased sensitiveness of the magnesium test. The whole solution is used for the test and therefore almost all of the magnesium contained in the original solution is involved. The precipitation of magnesium as the double phosphate takes place in a volume which can easily be made proportional to the amount of residue from the ammonium hydroxide extraction. Hence, the magnesium ammonium phosphate which tends to remain in supersaturated condition is more easily precipitated. The time of operation is no longer than that required for any scheme which involves the precipitation of magnesium by barium hydroxide and the subsequent removal of the latter. A disadvantage lies in the fact that the sulfate ion, which is not expelled by boiling with nitric acid, interferes, since magnesium sulfate is not readily decomposed to the oxide and remains water-soluble. It seemed possible at first that in the course of analysis sufficient hydrogen sulfide might be oxidized to sulfate to cause the latter's presence in every solution analyzed. However, in a test analysis this was not found to be the case. Violent ignition of magnesium sulfate with alkali sulfates was found by Debray[1] to yield magnesium oxide, but this temperature could hardly be obtained by students in elementary qualitative analysis. Precht and Wittjen[2] found it possible to separate magnesium sulfate from alkali sulfates by ignition with starch, whereby water-soluble alkali sulfides and insoluble magnesium oxide resulted.

Experimental Part

A solution was made containing approximately 5 mg. each of magnesium, sodium and potassium per cc. as nitrates. Twenty-five cc. portions of this solution were evaporated to dryness and the magnesium was separated from the alkalies by the method outlined above. After the separation magnesium was determined both in the ammoniacal filtrate and in the residue after the treatment with ammonium hydroxide. Magnesium was also determined in the original solution.

TABLE I

ANALYSES

	I	II	Av.
$Mg_2P_2O_7$ from 25 cc. of original solution, g.	0.2129	0.2128	0.2128
$Mg_2P_2O_7$ from NH_4OH residue, g.	.1968	.1990	.1979
$Mg_2P_2O_7$ from NH_4OH extract, g.	.0021	.0023	.0022
Residue by drying 25 cc. of solution and igniting until NO_2 fumes just cease to be evolved, g.	1.7575	1.7597	1.7586
Original Mg contd. in NH_4OH residue, %			93.00
Original Mg contd. in NH_4OH extract, %			1.03
Total			94.03

The discrepancy in the amount of magnesium started with and the amounts found in the ammoniacal extract and residue was probably due to unavoidable loss by spattering during ignition. The fused mass frothed a great deal and the bursting bubbles undoubtedly ejected some of the material, since a flame held over the evaporating dish was colored deeply by sodium. Covering the dish to catch the spatters did not prove effective since the bubbles swelled until they made contact with the cover and then ran over the dish and considerable material was lost. Only by very careful heating and by breaking the large bubbles with a point of flame could consistent results be obtained. This carefulness is, of course, unnecessary

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[1] Debray, *Compt. rend.*, **52**, 985 (1861).

[2] Precht and Wittjen, *Z. anal. Chem.*, **22**, 81 (1883).

for a qualitative separation and was taken only to secure semi-quantitative results.

To ascertain the sensitiveness of this separation the following experiments were performed. A solution containing 0.2 mg. each of magnesium, sodium and potassium as nitrates was evaporated, ignited and separated by means of dil. ammonium hydroxide. Positive tests for sodium and potassium were easily obtained from the ammoniacal filtrate and within ten minutes the residue from the ammonium hydroxide, after being dissolved in hydrochloric acid and made ammoniacal, gave a precipitate with sodium phosphate solution. A mixture of 50 mg. of potassium and 0.2 mg. of magnesium was separated by this method and a positive test for the latter was obtained. When 0.2 mg. of potassium was separated from 50 mg. of magnesium it yielded as the cobaltinitrite a faint precipitate, about one-tenth of the amount which 0.2 mg. gave directly. When magnesium nitrate was ignited and treated with ammonium hydroxide the extract failed to give a noticeable precipitate with potassium pyro-antimoniate; hence, interference of magnesium in the sodium test is prevented.

Summary

A simple, almost quantitative separation of magnesium from sodium and potassium can be accomplished by igniting the nitrates. When 0.2 mg. of any one of the three is present in the solution to be tested, it can be detected in the presence of the others even though the latter are in great excess.

The operation requires no more time than the usual scheme of separation.

Salts of acids whose salts are not decomposed to the oxide by ignition should be converted to nitrates by evaporating with nitric acid. Of the common anions that are likely to be present and interfere with the complete separation, sulfate alone cannot be readily expelled by the nitric acid. While the scheme of separation proposed here could be modified to take care of this ion by the method suggested by Precht and Wittjen,[2] no quantitative experiments were made along this line. The interference of the sulfate ion only arises when sulfate is present in the original. In the course of an analysis insufficient sulfate is formed by oxidation of the hydrogen sulfide to cause interference.

ORONO, MAINE