and an empirical factor determined. Otherwise, solution and reprecipitation of the phosphomolybdate precipitate are essential.[1]

## Conclusions.

The precipitate of ammonium phosphomolybdate formed in the presence of sulfuric acid (as in Neumann's method) contains sulfate apparently as an essential part of the molecule, together with an excess of molybdic oxide, and no nitric acid. The composition of this phosphosulfomolybdate precipitate may vary with the concentration of the different constituents in the solution. These variations explain the different factors found for the titration of the precipitate with alkali. The composition of the precipitate for a certain set of conditions was found to be $4[(NH_4)_3PO_4.12MoO_3] + (NH_4)_2SO_4.5MoO_3$.

# FLUOBORIC AND FLUOSILICIC ACIDS IN THE QUALITATIVE ANALYSIS OF SODIUM.

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The scheme for the detection of sodium is the only unsatisfactory test in the qualitative analysis of the soluble or alkali group of bases. The flame or spectrum test is so delicate that the quantity of sodium normally present in all reagents always distinctly gives it. This is confusing to inexperienced students. The pyroantimonate method has never given accurate results in this laboratory in the hands of beginning students. The following method is the final result of experiments which have been conducted by the authors for a number of years in an effort to devise a quick and accurate test for sodium.

**Method of Analysis.**—The filtrate containing the potassium, sodium, ammonium and magnesium (after the other metals have been removed in the ordinary way) is evaporated to dryness and ignited to remove the ammonium. The residue is dissolved in 10 cc. of water[2] by warming. A small portion of the solution (a few drops) is removed and tested for potassium with sodium cobaltic nitrite. The remainder of the solution is treated with an equal volume of alcohol and an excess of fluoboric acid in 50% alcohol. The potassium is completely precipitated as potassium fluoborate, a flocculent, easily filtered precipitate. Sodium and magnesium remain in solution. The sodium in the filtrate may then be precipitated with fluosilicic acid as sodium fluosilicate, a gelatinous, semi-transparent precipitate which settles slowly, consequently careful observation is necessary to detect it when only small quantities of sodium are present.

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[1] Cf. Hibbard, Raper, and others.

[2] Ten cc. of water should be used for each gram of sodium and potassium chloride present.

Magnesium fluosilicate, a very soluble salt, does not precipitate, but potassium fluosilicate and sometimes ammonium fluosilicate are precipitated if the potassium and ammonium have not been previously removed. In the absence of sodium, a precipitate sometimes forms on long standing as a result of the action of hydrofluoric acid upon the glass, if any free hydrofluoric acid was present in the reagents.

Lithium does not interfere with the test for sodium, probably on account of slow precipitation or colloidal solution of the lithium fluosilicate of which only 4 parts dissolve in 100 of 46% alcohol (Comey). In some test solutions rich in lithium, a gel formed after 48 hours.

**Preparation of Reagents.**—Fluoboric acid is very easily made by adding an excess of boric acid to hydrofluoric acid in a lead or platinum dish. Thirty-five grams of boric acid to 100 g. of 48% hydrofluoric acid is generally sufficient, but boric acid should always be added until a test portion does not precipitate a lead nitrate solution. The solution, after cooling, is treated with an equal volume of alcohol and enough fluosilicic acid to precipitate any sodium which may have been introduced as an impurity in the boric acid. A large excess of the fluosilicic acid must be avoided.

Fluosilicic acid may be easily prepared by pouring hydrofluoric acid upon sand until the latter is barely covered. A wax bottle may be used because the heat of reaction is not great. The reaction is complete in a few hours but the solution should always be tested for free hydrofluoric acid. An equal volume of alcohol should be added before using.

The reagents must be kept in wax, rubber, lead or paraffin bottles or beakers. In the ordinary course of analysis, these reagents when properly made, do not noticeably etch the test tubes.

These reagents work just as satisfactorily when made from commercial as from pure hydrofluoric acid. The only difficulty is in the preparation where the impurities, *e. g.*, sulfates, interfere with the test for fluoride in determining the completeness of the change into fluoboric and fluosilicic acids.

**Delicacy of Tests.**—One milligram of sodium in 5 cc. of 50% alcohol gives a good test with fluosilicic acid. In the detection of smaller amounts of sodium, a smaller volume of solution must be used. If large amounts of potassium and only small amounts of sodium are present, the filtrate after the precipitation of the potassium with fluoboric acid, should be evaporated to dryness and ignited for an instant at a dull red heat. The residue should be dissolved in 50% alcohol (2–3 cc.), filtered and tested for sodium with the fluosilicic acid. In this way 2 mg. of sodium in 0.5 g. of potassium chloride was easily detected. Addition of 1 g. magnesium chloride in no way interfered with the test for the sodium. Corresponding solutions containing no sodium gave no precipitate with the fluosilicic acid.

One mg. of sodium in 5 cc. of 50% alcohol was easily detected in a solution containing 0.1 g. of lithium as chloride and also in a solution containing 0.1 g. of lithium as chloride and 0.2 g. of potassium chloride. A blank, containing only lithium, gave no precipitate.

Pure fluoboric acid in 50% alcohol solution may be used as a test for potassium in place of sodium cobaltic nitrite or perchloric acid. Two milligrams of potassium in 5 cc. of 50% alcohol may be easily detected. The only objection to this test is that impure fluoboric acid, *e. g.*, when made from commercial hydrofluoric acid, sometimes gives a precipitate when potassium is absent; the cause of this was not investigated. The advantage of this test is that it is not interfered with by sodium and magnesium nor by ammonium and cyanides which interfere with the sodium cobaltic nitrite test. However, owing to the trouble of making pure fluoboric acid, the test for potassium with sodium cobaltic nitrite seems best wherever it can be used.

**Use of Other Reagents.**—Perchloric acid[1] is preferable to the fluoboric acid in this method but the latter is recommended because it is so much easier to prepare.

Oxalic acid in 50% alcohol solution gives a delicate test for sodium, but no rapid method was found of removing the interfering potassium, without introducing free acid which prevents the precipitation of the acid sodium oxalate.

Potassium fluozirconate in 50% alcohol solution, is a delicate reagent for sodium, but potassium solutions also precipitate it.

Tartaric acid in 50% alcohol solution does not completely precipitate the potassium in potassium chloride because of the free mineral acid that is simultaneously formed, hence tartaric acid cannot be used in place of the fluoboric acid.

The advantages of this new method are:

1. Tests may be made in the presence of magnesium, the removal of which, generally a long difficult task, is necessary if the potassium pyroantimonate nethod is to be used.

2. The reagents are comparatively cheap and are very easy to prepare.

3. The reactions and equations are simple and easily understood, and only a short time is required to make an analysis.

4. The test is decisive, and the student has confidence in his work. A large class of inexperienced students obtained very accurate results in a trial of the method lasting two terms.

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[1] Mathers and Lee, *Indiana Univ. Studies*, **9**, 180 (1912).