269.—*The Elimination of the Phosphate Radical in Qualitative Analysis.*

By L. W. N. Godward and A. M. Ward.

A number of processes have been described to overcome interference of the phosphate radical in qualitative inorganic analysis (for references, see Smith, J., 1933, 253; *Ann. Reports*, 1936, **33**, 451); Smith (*loc. cit.*) also developed an improved scheme, based on precipitation from a buffered formate solution (see also Tower, *J. Amer. Chem. Soc.*, 1910, **32**, 953; Schulze, *Centr.*, 1861, 3). No process appears to have been described in which phosphate is eliminated as ammonium phosphomolybdate; the present paper contains a fairly concise scheme based on this, and includes the detection of calcium as its molybdate. Ammonium molybdate may not have been used in this way previously, for molybdenum is often considered among the "rarer" elements; ammonium molybdate is, however, less expensive than many compounds which, by usage, are regarded as "common." Nevertheless, in the procedure which follows, only "common" elements in the classical schemes of analysis are included.

Phosphate Separation.

After Group II, boil off H_2S, oxidise with concentrated HNO_3 (1—2 ml.). To one part (½ ml.) add concentrated HNO_3 (1 ml.) and ammonium molybdate solution (4—5 ml.) and warm : yellow precipitate = *Phosphate.* To a second portion (½ ml.) add ammonium chloride (0·5 g. in 3 ml. water) and ammonia : if no precipitate forms, or a precipitate soluble in excess, proceed to zinc group with main bulk of solution; if precipitate is insoluble in excess of ammonia, to main bulk of solution add a few ml. of dilute H_2SO_4 and about 1 g. of $(NH_4)_2SO_4$. Boil and filter.

<table>
<tr><td colspan="2" rowspan="3"><i>Precipitate.</i>—$SrSO_4$ and $BaSO_4$. Boil for 3—4 mins. with 10 g. of Na_2CO_3 and 50 ml. of water. Filter and neglect filtrate. Dissolve ppt. in acetic acid, filter (neglect insol. part, $BaSO_4$). Add K_2CrO_4. Filter.</td><td colspan="4"><i>Filtrate.</i>—Dilute to about 25 ml. with water, add 5 ml. of conc. HNO_3 and 5 g. of NH_4NO_3. Boil, and stir in powdered ammonium molybdate until present in excess (see Note 2). Boil for 5 mins., filter, and reject ppt. Heat a small portion of filtrate with ammonium molybdate to ensure that all phosphate is removed. To the cooled filtrate, add NH_4OH (<i>d</i> 0·880) dropwise with cooling until present in very slight excess. Filter.</td></tr>
<tr><td rowspan="3"><i>Precipitate.—Ferric, aluminium,</i> and <i>chromium hydroxides.</i> Confirm by usual group procedure.</td><td colspan="3"><i>Filtrate.</i>—Make ammoniacal, and pass H_2O. Filter, and wash ppt. well with hot water.</td></tr>
<tr><td rowspan="2"><i>Precipitate.—Zinc, cobalt, nickel,</i> and <i>manganese sulphides.</i> Confirm by usual group procedure.</td><td colspan="2"><i>Filtrate</i> (orange).—Acidify with HCl, boil off H_2S, filter. Reject ppt. of molybdenum sulphide. To filtrate, add sodium perborate and sodium hydroxide solution. Boil until solution colourless, and continue boiling for a few minutes to destroy excess perborate (see Note 5). Acidify with HCl, boil, filter, make ammoniacal, add 5 g. of NH_4OAc and 10 ml. of ammonium molybdate solution.* Boil gently for 10 minutes. Filter.</td></tr>
<tr><td><i>Precipitate.</i>
Yellow = <i>barium.</i></td><td><i>Filtrate.</i>
Add dil. H_2SO_4.
White ppt. = <i>strontium.</i></td><td><i>Precipitate.</i>—White $CaMoO_4$. Confirm <i>calcium</i> by dissolving ppt. (readily) in hot dilute sulphuric acid, and reprecipitating by addition of ammonia and ammonium oxalate.</td><td><i>Filtrate.</i>—Add solution of <i>p</i>-nitrobenzeneazoresorcinol, followed by NaOH until colour of dye changes. Blue gelatinous ppt. = <i>magnesium.</i></td></tr>
<tr><td colspan="2">See Note 1.</td><td>See Note 3.</td><td>See Note 4.</td><td>See Note 6.</td><td></td></tr>
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To test for sodium and potassium : proceed by the usual group separations adopted when phosphate is absent, and examine for these two metals in the usual way.

* A 6% solution of ammonium molybdate in dilute ammonia.

Notes on the Procedure.—(1) Barium and strontium are precipitated before the addition of considerable quantities of ammonium salts, which markedly increase the solubilities of the two sulphates. In presence of large amounts of calcium, some calcium sulphate may be precipitated at this stage; it does not, however, interfere with the confirmatory tests for barium and strontium, and sufficient will remain in solution for the subsequent precipitation of calcium molybdate.

(2) Powdered ammonium molybdate is used on account of the large proportion needed to precipitate the phosphate radical [1 g. PO_4''' = 22·15 g. $(NH_4)_6Mo_7O_{24},4H_2O$]. With this in view, if for no other reason, large amounts of substance should not be taken for analysis; unless traces are being sought, 0·2 g. of material is usually sufficient.

Boiling for 5 minutes serves, not only to complete the precipitation of phosphomolybdate, but also to remove any molybdic acid which might be precipitated during subsequent heating. The precipitation of the phosphate, and indeed most of the reactions in the scheme, can conveniently be carried out in 100 ml. beakers. Excess of molybdate is clearly denoted by the presence of white, insoluble molybdate, mixed with the yellow phosphomolybdate.

(3) Concentrated ammonia is used for the precipitation of the iron group in order to avoid

excessive dilution, but it is added only in the slightest excess. The solution is kept cold to prevent possible precipitation of calcium as molybdate.

(4) Adsorption of molybdenum compounds on the precipitate of zinc, cobalt, nickel, and manganese sulphides is sometimes tenacious. Prolonged passage of hydrogen sulphide, with consequent reduction of the molybdate solution, and increased adsorption, should be avoided. It is occasionally best to dissolve the sulphides and reprecipitate them.

(5) Before testing for magnesium, hydrogen sulphide must be removed, as it decomposes *p*-nitrobenzeneazoresorcinol. It is also best to oxidise the coloured molybdenum compounds to colourless Mo^{VI}, for the formation of the blue lake is more easily observed in a colourless solution.

(6) Calcium is dealt with separately as molybdate, a point which we consider to be of considerable value. The presence of ammonium acetate diminishes the rate of precipitation of calcium molybdate and amounts larger than 5 g. should be avoided. Its presence is, however, necessary to prevent precipitation of molybdic acid.

Remarks.—During the development of the scheme, the precipitation of magnesium, zinc, cobalt, and nickel in presence of molybdenum by means of oxine in ammoniacal solution, was examined (Fleck and Ward, *Analyst*, 1933, **58**, **388**); it was found, however, to be unsatisfactory as a qualitative procedure.

Test analyses have been made of mixtures containing selections of all the elements considered in various proportions; in all cases the procedure afforded good qualitative separations. Traces were not usually sought, for precipitations must be carried out from solutions more dilute than those used in this scheme if adsorption by precipitates is to be avoided.

THE MUNICIPAL COLLEGE, PORTSMOUTH.

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