A Rearrangement of Procedure for the Removal of Phosphate Ions from the Iron and Alkaline Earth Groups.

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The following procedure is the result of several attempts to simplify the various methods in common use for the removal of phosphate ions during the qualitative separation of the metals of the iron and alkaline earth groups. It has been the author's experience that, for the usual college class in qualitative analysis, the methods commonly used require rather too much nicety in manipulation to be altogether practicable. The procedure given below has been used by the class in qualitative analysis at Dalhousie University this year with very favorable results.

1. *Procedure.*—Treat the solution (after the removal of all the metals precipitated by H_2S in acid solution) with a few drops of conc. HNO_3 and boil until all H_2S is expelled; filter if necessary. Add at once about ⅓ volume of strong NH_4Cl solution and a *slight* excess of NH_4OH. Filter:

Notes.—1. The HNO_3 is added to oxidize any iron that may be present, which after the H_2S treatment is always in the ferrous condition.

2. The treatment with HNO_3 may also cause a slight precipitation of sulphur from the H_2S.

3. Care must be taken to avoid adding more than a slight excess of NH_4OH, since the precipitate of $Al(OH)_3$ is somewhat soluble in an excess.

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3. The precipitate with NH_4OH under ordinary conditions would consist only of hydroxides of Fe, Al and Cr. If however PO_4''' ions are present, it may also contain phosphates of the above metals and also of Ca, Ba, Sr and Mg.

2. *Procedure.*—Dissolve a small portion of the NH_4OH precipitate in HNO_3 (Sp. g. 1.2) and test for PO_4''' ions with $(NH_4)_2 MoO_4$. If a yellow precipitate forms, dissolve the remaining portion of the precipitate in dilute HCl (Sp. g. 1.12). Test a small portion of the solution for Fe with $K_4Fe(CN)_6$. To the remaining solution add $FeCl_3$ solution, drop by drop, until (after careful stirring), a drop of the solution removed by means of a stirring rod gives a *brown* precipitate of $Fe(OH)_3$ with NH_4OH on a porcelain plate.

Notes.—1. The test for Fe must be made at this point since $FeCl_3$ is added to the solution later on.

2. The addition of $FeCl_3$ causes a precipitation of $FePO_4$ (white) when the solution is made alkaline by NH_4OH. When a sufficient amount of $Fe^{\cdot\cdot}$ ions has been added to combine with all PO_4''' ions, an excess of $FeCl_3$ causes a precipitation of the brown $Fe(OH)_3$.

3. *Procedure.*—To the HCl solution containing an excess of $FeCl_3$ add NH_4Cl solution and a slight excess of NH_4OH. Filter. Save the filtrate.

Notes.—1. After the addition of NH_4OH, the precipitate will contain, $FePO_4$, and hydroxides of Fe, Cr, and Al, all the PO_4''' ions remaining in the precipitate. The filtrate may contain ions of Mn, Ni, Co, Ba, Sr, Ca, and Mg.

4. *Procedure.*—Dissolve the above precipitate in dilute HCl (Sp. g. 1.12) and add an excess of NaOH and H_2O_2. Filter.

Notes.—1. By the addition of NaOH and H_2O the $Al(OH)_3$ is converted into the soluble Na_3AlO_3, and the $Cr(OH)_3$ is oxidized to Na_2CrO_4, the iron precipitate remaining behind on the filter.

5. *Procedure.*—Divide the above solution into two parts, and to one add an excess of $HC_2H_3O_2$ and a few cc. of $Pb(C_2H_3O_2)_2$ solution. A yellow precipitate indicates Cr. To the other portion add an excess of dilute H Cl, and then a slight excess of NH_4OH. Warm and set aside. A white flocculent precipitate is $Al(OH)_3$.

6. *Treatment of filtrate from* 1.—Acidify a small portion of the solution with dilute HNO_3 and test for PO_4''' ions with $(NH_4)_2MoO_4$ If a yellow precipitate is formed, treat the remainder of the solution with H_2S. A white precipitate is ZnS. If no PO_4''' ions are found, see 7.

Notes.—1. The addition of even a slight excess of NH^4OH in 1, is sufficient to convert the Zn into the soluble complex compound $Zn(NH_3)_4(OH)_2$, which passes through into the filtrate and is removed by H_2S.

2. If the addition of $(NH_4)_2MoO_4$ shows the presence of PO_4''' ions, then the solution after the removal of Zn contains only the metals of the alkali group.

7. *Procedure.*—If PO_4''' ions are not found in 6, add solution to filtrate from 3, warm, and to the warm solution add an excess of H_2S. Filter:

Notes.—1. If PO_4''' ions are not found in 6, the solution will contain only those ions in excess of what was necessary to combine with the PO_4''' ions precipitated in 1. They may consist of: Zn, Mn, Ni, Co, Ba, Sr, Ca, Mg, K and Na.

8. *Procedure.*—Treat precipitate with a small amount of dilute H Cl (1 part H Cl 1.12 to 5 parts water). Residue may be Ni S and Co S. Separate in usual way. Treatment of

H Cl solution: Add an excess of Na O H. Filter and fuse the precipitate with Na_2CO_3 on platinum foil. Green color indicates Mn. To filtrate add H_2S. White precipitate is Zn S.

Notes.—1. An excess of Na OH forms a soluble compound with the Zn, Na_2 Zn O_2, which passes into the filtrate. The Mn is at the same time precipitated as Mn $(OH)_2$ and converted by fusion with Na_2CO_3 to the compound Na_2MnO_4, which is green in color.

9. *Procedure.*—The filtrate from 7 now contains only the ions of the alkaline earth and alkali groups. These are separated and identified in the usual manner.