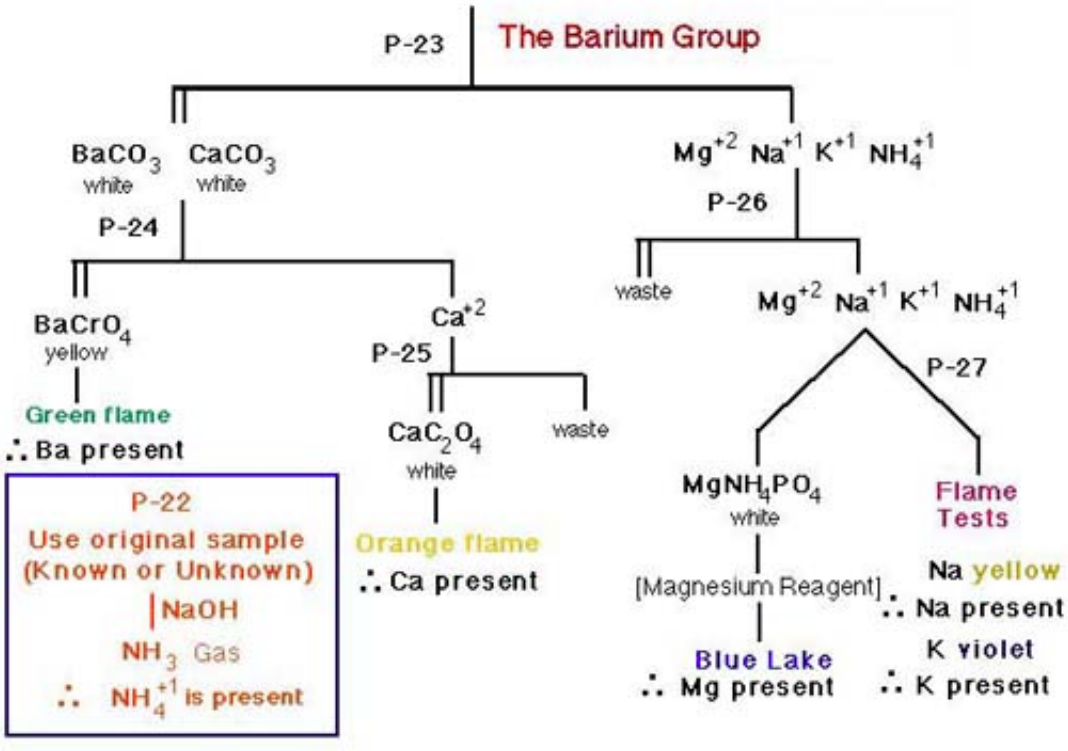
The Barium Group



After removal of the preceding groups, the ions of Barium, Calcium, Magnesium, Potassium, Sodium, and Ammonium remain in the solution being analyzed. Barium and Calcium are members of the Barium subgroup. The remaining four will be called the Magnesium subgroup.

Detection of Ammonium Salts:

Facts: When an Ammonium salt is heated with a strong base, Ammonia gas is evolved. This fact is the basis for the detection of Ammonium. Since NH_4Cl, as well as other Ammonium salts, is added at various points in the cation analysis, the test for Ammonium must be made on a sample of the original material.

Procedure 22: Detection of Ammonium

Place 5 drops of 8 M NaOH [hood] in a test tube. Add 5 drops of the original solution to be tested (Either a known [E-11] or unknown from instructor). Warm gently but do not boil. The evolution of NH_3 gas, detected by its odor or by its reaction to a piece of moist red litmus held down in the mouth of the tube, proves the presence of Ammonium compounds.

.

Precipitation of Calcium and Barium

The separation of Barium and Calcium ions from the cations of the Magnesium subgroup depends on the fact that, in an alkaline solution containing excess NH_4^{+1} ions, Calcium and Barium are precipitated as $CaCO_3$, and $BaCO_3$, whereas Magnesium, Sodium, and Potassium ions remain in solution.

The instructor, or an experienced student, will show you how to flame test.

Procedure 23: Precipitation of Calcium and Barium

If the solution to be analyzed is a Barium group ***known*** [E-11] or ***unknown*** [from instructor], follow Method (A) below. If the decantate from Procedure 15 is being analyzed in a salt analysis, follow Method (B). [WARNING: Never mix the ***known*** with the ***unknown!***]

(A) Place 6 drops of the solution to be analyzed in a test tube and add 6 drops of cold water. Then add 4 drops of 2 M NH_4Cl [B-7], mix thoroughly, make alkaline with 15 M NH_4OH [A-8], and add 2 M $(NH_4)_2C0_3$ [B-6] until precipitation is complete (5 drops is generally sufficient).

Heat in the water bath for 1 minute, then cool. When precipitation is complete, centrifuge and decant, saving the decantate for Procedure 26.

Wash the precipitate ($CaC0_3$, $BaC0_3$) three times with cold water and analyze according to Procedure 24.

(B) Place the decantate from Procedure 15 in a crucible, evaporate to a volume of 8 drops, transfer to a test tube, and centrifuge.

Decant into a crucible, discarding any precipitate. Add 6 M HCl [A-2] until the solution is slightly acidic; then evaporate to dryness and bake until absence of further sublimation indicates that all Ammonium salts are driven off. Allow to cool.

Then add 12 drops of hot water and stir for 1 minute. Transfer the solution to a test tube; if the solution is clear (no solid in it), proceed as directed in (A) above. If the solution is not clear, then centrifuge, decant the clear supernatant liquid into a test tube, and proceed with it as directed in (A) above.

Separation of Barium from Calcium

Facts: Calcium chromate is quite soluble in dilute acetic acid. Barium chromate is relatively insoluble. Upon these facts is based the separation of Barium ions from Calcium ions.

.

Procedure 24: Separation and detection of Barium

Dissolve the precipitate from Procedure 23 in 3 drops of 2 M HC1 [A-3].

Make just alkaline with 5 M NH_4OH [A-9], then just acid with 5 M $HC_2H_30_2$ [A-7] and then add 1 drop of 5 M $HC_2H_30_2$ [A-7], 4 drops of water, and 1 drop of 0.2 M K_2Cr0_4 [D-1].

If no precipitate forms, Barium is absent. In that case analyze the solution according to Procedure 25.

If a **yellow** precipitate ($BaCrO_4$) forms, Barium is present; in that case add K_2Cr0_4 [D-1] until precipitation is complete.

Centrifuge; save the decantate for Procedure 25. Dissolve the washed $BaCrO_4$ in 2 drops of 6 M HCl [A-2], add 2 drops of 2 M H_2S0_4 [A-5]. Centrifuge and wash the precipitate ($BaS0_4$) three times with water. Add 3 drops of 12 M HCl [Hood], mix, and make a flame test on this mixture. A **green** flame proves the presence of Barium.

Procedure 25: Detection of Calcium

Make the decantate from Procedure 24 (or, if Barium is absent, the solution from Procedure 24) just alkaline with 15 M NH_4OH [A-8]. Then add 5 drops of 0.2 M $(NH_4)_2C_2O_4$, Ammonium oxalate, [B-10]. A white precipitate (CaC_2O_2) proves the presence of Calcium.

Centrifuge and decant, discarding the decantate. Wash the precipitate three times with hot water, dissolve it in 6 M HCI [A-2], and run a flame test. An **orange-red** flame further proves the presence of Calcium.

Procedure 26: Separation and detection of Magnesium

Treat the decantate from Procedure 23 with 2 drops of 0.2 M $(NH_4)_2SO_4$ [B-11] and 2 drops of 0.2 M Ammonium oxalate, $(NH_4)_2C_2O_4$ [B-10], heat to boiling. Allow to cool, centrifuge, and decant, discarding any precipitate ($BaS0_4$, CaC_20_4).

Save one half of the decantate for the detection of Sodium and Potassium, Procedure 27. Treat the other half with 1 drop of 5 M NH_40H [A-9] and 4 drops of 0.2 M Na_2HP0_4, Disodium phosphate, [C-4] mix well, warm gently, and allow to stand for 1 minute.

A white precipitate ($MgNH_4P0_4$) shows the presence of Magnesium, but...

Do this, too, and be able to pronounce the name of the magnesium reagent:

Centrifuge and decant, discarding the decantate. Wash the precipitate three times with hot water, dissolve in 3 drops of 2 M HCI [A-3], and then add 4 drops of ***The Magnesium Reagent*** [C-10], (**paranitrobenzeneazoresorcinol**). [To re-fill the bottle, search under ***Magnesium Reagent***].

Then add 8 M NaOH [hood], with constant mixing, until the solution is distinctly alkaline, and centrifuge. A ***blue lake*** **(flocculent precipitate)** proves the presence of Magnesium. (Flocculent means flaky, like the "snow" in a crystal ball).

Procedure 27: Detection of Sodium and Potassium

Evaporate the remaining half of the decantate from Procedure 26 to dryness and bake in the crucible at the maximum temperature of the fiame until the absence of white smoke or vapor indicates that all NH4Cl has sublimed off.

If there is no solid residue in the crucible, Sodium and Potassium are absent.

Alow to cool, then treat the solid residue with 2 drops of 6 M HCI [A-2], and make a flame test.

A fluffy yellow flame proves the presence of sodium.

A quick flash of lavender flame, viewed through a ***blue glass filter plate***, proves the presence of Potassium. The blue filter is to hide the big yellow flame of sodium which may cover the lavender. Be sure not to confuse the glowing test wire with the lavender flame!

Here Endeth the Barium Group