Experiment 3: The Qual Scheme
Selected Cations in Group IV

Note: Procedures start with Procedure 19, rather than Procedure 1 because this is part of an extensive qual scheme containing Cation Groups I, II, III, and IV. We did not investigate Groups II and III, and will examine only three of the five cations in Group IV.

In Proc 19 we test for the presence of the ammonium ion outside the flow of the qual scheme. The test depends on the volatility, thus mobility, of NH_3 which is readily formed from NH_4^+.

$$NH_4^+(aq) \; + \; 8M \;\; NaOH \;\; \rightarrow \;\; NH_3 \uparrow \; + \; H_2O \; + \; Na^+$$

$$NH_3 \; + \; H_2O \;\; \rightarrow \;\; NH_4^+ \; + \; OH^- \; (\text{litmus} \rightarrow \text{blue})$$

Barium is separated in Proc 20 by precipitation as the sulfate.

$$Ba^{2+}(aq) \; + \; 0.2M \;\; (NH_4)_2SO_4 \;\; \rightarrow \;\; \underset{\text{white}}{\underline{BaSO_4}} \; + \; 2 \;\; NH_4^+$$

Calcium is separated in Proc 21 by precipitation as the oxalate, then dissolved for the flame test.

$$Ca^{2+}(aq) \; + \; 0.2M \;\; (NH_4)_2C_2O_4 \;\; \rightarrow \;\; \underset{\text{white}}{\underline{CaC_2O_4}} \; + \; 2 \;\; NH_4^+$$

$$CaC_2O_4 \; + \; 6M \;\; HCl \;\; \rightarrow \;\; Ca^{2+} \; + \; 2 \;\; Cl^- \; + \; H_2C_2O_4$$

Flame Test Procedures

Your flame tester consists of a 2 – 3 inch piece of nichrome wire with one end fused into a glass rod to act as a handle. The other end is shaped into a loop of about 2-mm diameter. If dipped into an aqueous liquid solution, the loop will support a thin film of the liquid.

Use a small but hot flame for the test (usually the hottest part). Position yourself so that the flame has a background of the black bench top. Then dip the wire loop in the solution to be tested and in to the flame; watch for color. Be patient and just keep doing it.

We rely on flame test for barium and calcium. Sodium (which is also in Group IV but for which we are not testing) gives *fluffy* yellow (to orange) flame and is so intense and persistent that when it is present all other flame tests are hard (or impossible) to see. Aqueous solutions, on standing in glass containers, will leach sodium ions from the glass and give a positive sodium flame test.
The 'apple' green barium flame is also easily seen in the absence of sodium but is difficult with sodium present. In Proc 20 you will try to dissolve washed $BaSO_4$ for a flame test. The washing is to reduce the sodium present. However, $BaSO_4$ is scarcely soluble and you will need to flame it

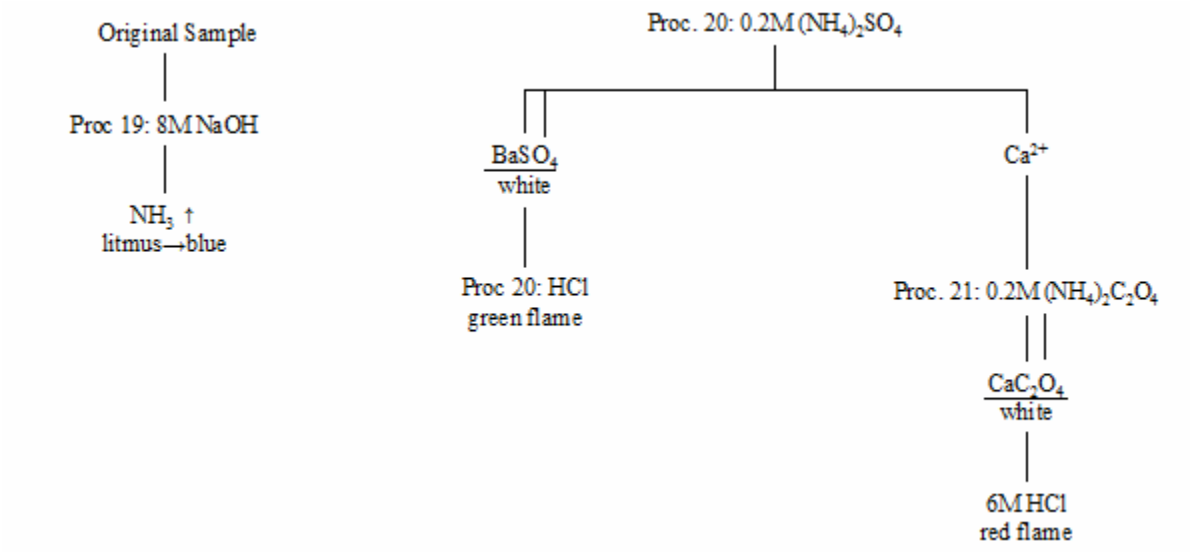
repeatedly. After several tries, barium (probably as the oxide) often tends to build up on the wire making the test easier to see.

The calcium flame is a distinct brick-red but always of short duration and seems to sputter. However, if you allow calcium oxide to build up on the wire through several flamings, then dip once into l2M HCl, this often gives a more intense and more persistent test.

When starting flame test you should clean your wire thoroughly with l2M HC1 a couple of inches deep in a test tube, repeatedly dipping and burning for a sustained period until the yellow-orange sodium flame is minimized and no other flame color is noted. If your wire becomes too dirty you could clip off the worst part and role yourself another loop or install a new piece of wire.

Flow Diagram for Group IV : 19-21

Ba^{2+}, Ca^{2+}, NH_4^+
(all colorless)



Group IV Procedures

Procedure 19

The test for ammonium ion is performed on the most original, unadulterated, sample you have. We will do the procedure so as to include a reagent blank test. Using a clean casserole mix a few drops of water and a few drops of 8M NaOH. Cover this with a watch glass which has a wet piece of red litmus stuck to it on the bottom so it faces the solution in the bottom of the casserole. Now warm the casserole by holding it over your water bath (do not heat on direct flame). Now watch the litmus paper; if it turns blue in under a minute there is too much NH_3 in the air or in your reagents. If not, lift the watch glass and drop in a few drops of the solution to be tested. The litmus should turn blue smoothly, starting from the edges, within 30 seconds for a positive ammonium test.

Note: An astounding number of students either use a sample to which an ammonium reagent has been added or use NH_3 instead of NaOH in the procedure.

Procedure 20

This is a good time to do a flame test on your Group IV sample. Consult the special section on flame tests just prior to Proc 19. Use 6 drops of a Group IV sample.

Add a single drop of 0.2M $(NH_4)_2SO_4$, mix and look for the beginnings of white precipitate. Add one more drop; if there is still no precipitate present, there is no Ba^{2+}. Take the solution on to Proc 21. If a precipitate, $BaSO_4$, shows up, centrifuge and test for complete precipitation by sliding in one more drop of $(NH_4)_2SO_4$ solution. Do not add more than 4 drops altogether. Centrifuge, decant, and take the decantate to Proc 21. Wash the precipitate with two 10-drop portions of hot water to free it of sodium ion. Attempt to dissolve the washed precipitate in 3 drops of 12M HC1, with heating and stirring. Do a flame test for barium. However, you will proba1y have to depend on the white precipitate to prove the presence of Ba^{2+}.

Procedure 21

Test the decantate from Proc 20 by first adjusting its pH to just basic (to litmus) by adding 5M NH_3 one drop at a time, testing after each drop. Then add 2 drops of 0.2M $(NH_4)_2C_2O_4$. If no c1oudiness appears, no calcium is present. If a white precipitate, CaC_2O_4, is seen, test for complete precipitation but limit the $(NH_4)_2C_2O_4$ additions to no more than 5 drops. Centrifuge, separate, and discard the decantate. Wash the precipitate twice with 10-drop portions of hot water then dissolve it in a minimal amount (2-3 drops) of 6M HC1 (kit). Flame test this solution to confirm the presence of Ca^{2+}.