QUALITATIVE ANALYSIS of GROUP III CATIONS

The four group III cations in this lab are \(\text{Cr}^{+3}\), \(\text{Al}^{+3}\), \(\text{Fe}^{+3}\), and \(\text{Ni}^{+2}\). The first step in analysis involves separating the ions into two subgroups by treating the solution with NaOH and NaOCl. The hypochlorite ion oxidizes \(\text{Cr(III)}\) to a higher, more stable oxidation state (namely \(\text{Cr(VI)}\)) which is soluble:

\[
2 \text{Cr}^{+3}(aq) + 3 \text{OCl}^{-1}(aq) + 10 \text{OH}^{-1}(aq) \rightarrow 2 \text{CrO}_4^{2-}(aq) + 3 \text{Cl}^{-1}(aq) + 5 \text{H}_2\text{O(l)}
\]

In addition, \(\text{Al}^{+3}\) forms a soluble hydroxo-complex ion in the presence of excess hydroxide:

\[
\text{Al}^{+3}(aq) + 4 \text{OH}^{-1}(aq) \rightarrow \text{Al(OH)}_4^{-1}(aq)
\]

In contrast, \(\text{Ni}^{+2}\) and \(\text{Fe}^{+3}\) do not readily form hydroxo-complexes and are not oxidized by hypochlorite. They form insoluble hydroxides under these conditions:

\[
\text{Ni}^{+2}(aq) + 2 \text{OH}^{-1}(aq) \rightarrow \text{Ni(OH)}_2(\text{green solid})
\]

\[
\text{Fe}^{+3}(aq) + 3 \text{OH}^{-1}(aq) \rightarrow \text{Fe(OH)}_3(\text{red solid})
\]

To separate aluminum from chromium, the solution containing \(\text{CrO}_4^{2-}\) and \(\text{Al(OH)}_4^{-1}\) is acidified to destroy the hydroxo-complex:

\[
\text{Al(OH)}_4^{-1}(aq) + 4 \text{H}^{+}(aq) \rightarrow \text{Al}^{+3}(aq) + 4 \text{H}_2\text{O(l)}
\]

Treatment with aqueous ammonia gives a gelatinous **white** precipitate of aluminum hydroxide. The concentration of hydroxide in ammonia is too low to form the hydroxo-complex:

\[
\text{Al}^{+3}(aq) + 3 \text{NH}_3(aq) + 3 \text{H}_2\text{O(l)} \rightarrow 3 \text{NH}_4^{+}(aq) + \text{Al(OH)}_3(\text{white solid})
\]

The chromate ion remains in solution. It can be tested and confirmed by precipitation as yellow \(\text{BaCrO}_4\):

\[
\text{Ba}^{+2}(aq) + \text{CrO}_4^{2-}(aq) \rightarrow \text{BaCrO}_4(\text{yellow solid})
\]

The \(\text{BaCrO}_4\) precipitate dissolves in acid. The solution is then treated with \(\text{H}_2\text{O}_2\) to produce a **deep blue** color due to the presence of a peroxo-compound, probably \(\text{CrO}_5\):

\[
2 \text{BaCrO}_4(s) + 4 \text{H}^{+}(aq) + 4 \text{H}_2\text{O}_2(aq) \rightarrow 2 \text{Ba}^{+2}(aq) + 6 \text{H}_2\text{O(l)} + 2 \text{CrO}_5(\text{blue, aq})
\]

The mixed precipitate of \(\text{Ni(OH)}_2\) and \(\text{Fe(OH)}_3\) can be dissolved by adding a strong acid. The \(\text{Ni}^{+2}\) and \(\text{Fe}^{+3}\) ions can be separated by adding ammonia. \(\text{Ni}^{+2}\) is converted to the deep-blue complex \(\text{Ni(NH}_3)_6^{+2}\) which stays in solution. The \(\text{Fe}^{+3}\) ion does not readily form a complex and re-precipitates as \(\text{Fe(OH)}_3\):

\[
\text{Ni}^{+2}(aq) + 6 \text{NH}_3(aq) \rightarrow \text{Ni(NH}_3)_6^{+2}(\text{blue, aq})
\]

\[
\text{Fe}^{+3}(aq) + 3 \text{NH}_3(aq) + 3 \text{H}_2\text{O(l)} \rightarrow 3 \text{NH}_4^{+}(aq) + \text{Fe(OH)}_3(\text{red solid})
\]

Confirm the presence of \(\text{Ni}^{+2}\) by adding dimethylglyoxime (DMG), \(\text{C}_4\text{H}_8\text{N}_2\text{O}_2\), to give a **deep rose** precipitate:

\[
\text{Ni}^{+2}(aq) + 2 \text{C}_4\text{H}_8\text{N}_2\text{O}_2(aq) \rightarrow 2 \text{H}^{+}(aq) + \text{Ni(C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{red solid})
\]

Confirm the presence of \(\text{Fe}^{+3}\) by dissolving \(\text{Fe(OH)}_3\) in a strong acid and adding KSCN to form a **blood-red** \(\text{FeSCN}^{+2}\) complex ion:

\[
\text{Fe}^{+3}(aq) + \text{SCN}^{-}(aq) \rightarrow \text{FeSCN}^{+2}(\text{red, aq})
\]
**PROCEDURE:** Be sure to include a flowchart with this lab report. **Safety glasses required for everyone, all the time - no open toed shoes or sandals, no shorts or mid-riff showing shirts.** This can be a longer lab, so come prepared and organized to maximize your lab experience.

**Step 1: Preparation:** If you are working on the analysis of only group III ions, prepare a known solution by mixing 5-6 drops each of 0.1 M solutions of Fe$^{3+}$, Al$^{3+}$, Cr$^{3+}$, and Ni$^{2+}$ in a 30 mL beaker. Also obtain an unknown to analyze at the same time for the presence of group III cations and use about 20-24 drops in your analysis.

**Step 2: Oxidation of Cr(III) to Cr(VI) and Separation of Insoluble Hydroxides:** Add 1 mL of 6 M NaOH to the solution in a 30 mL beaker. Boil very gently for 1 minute while stirring. Remove heat and slowly add dropwise 1 mL of 1 M NaClO. Swirl the beaker for 30 seconds, using tongs if necessary. Boil the mixture for 1 minute. Centrifuge. Transfer the supernatant (which contains the aluminum and chromate) to a separate tube. Wash the precipitate (which contains iron and nickel hydroxides) with 2 mL water and 0.5 mL of 6 M NaOH. Stir, centrifuge, decant and discard the wash. Add 1 mL of water and 1 mL of 6 M HNO$_3$ to the solid and put it aside until step 6.

**Step 3: Separation of Al from Cr:** Acidify the solution from step 2 by adding 6 M acetic acid in 10 drop increments until, after stirring, the mixture is definitely acidic to litmus. If necessary, transfer the solution to a 30 mL beaker and boil it to reduce its volume to about 3 mL. Pour the solution into a test tube. Add 6 M NH$_3$ in 5 drop increments until the solution is basic to litmus; and then add 0.5 mL excess. Stir the mixture for one minute to bring the system to equilibrium. If aluminum is present, a light, translucent gelatinous white precipitate of Al(OH)$_3$ may be floating in the clear to yellow solution. Centrifuge and transfer the liquid (which contains CrO$_4^{2-}$) to another test tube.

**Step 4: Confirmation of the Presence of Aluminum:** Wash the precipitate from step 3 with 3 mL water, warming the test tube in the water bath and stirring well. Centrifuge and discard the wash. Dissolve the precipitate in 2 drops of 6 M CH$_3$CO$_2$H (no more, no less!). Add 3 mL of water and 1-2 drops of aluminon. Stir. If Al$^{3+}$ is present, the solution will turn a lovely rose-pink color due to the presence of a very fine red or pink precipitate.

**Step 5: Confirmation of the Presence of Chromium:** A yellow liquid from step 3 suggests but does not confirm the presence of chromium. To the solution add 0.5 mL of 1.0 M BaCl$_2$. In the presence of chromium a finely divided yellow precipitate of BaCrO$_4$ appears. Put the test tube in boiling water for two minutes. Centrifuge and discard the liquid. Wash the solid with 2 mL of water, centrifuge and discard the wash. To the solid add 0.5 mL of 6 M HNO$_3$. Stir to dissolve BaCrO$_4$. Add 1 mL of water; stir the orange solution. Add 2 drops of 3% H$_2$O$_2$. A deep blue solution, which may fade rapidly, confirms the presence of chromium.

**Step 6: Separation of Iron and Nickel:** Returning to the precipitate from step 2, stir to dissolve the solid in the HNO$_3$. If necessary, warm the test tube in the water bath to completely dissolve the solid. Add 6 M NH$_3$ until the solution is basic to litmus. At this point, iron will precipitate as brown Fe(OH)$_3$. Add 1 mL more of the NH$_3$ and stir to bring the nickel into solution as the Ni(NH$_3$)$_6^{2+}$ ion. Centrifuge and decant the liquid into a test tube. Save the precipitate for step 8 to test for the presence of iron.

**Step 7: Confirmation of the Presence of Nickel:** If the solution from step 6 is blue, nickel may be present. To the solution add 0.5 mL dimethylglyoxime (DMG) reagent. Formation of a rose-red precipitate proves the presence of nickel.

**Step 8: Confirmation of the Presence of Iron:** Dissolve the precipitate from step 6 in 0.5 mL of 6 M HCl. Add 2 mL water and stir. Add 2 drops of 1.0 M KSCN. Iron is present if a deep red solution of FeSCN$^{2+}$ is formed.

**Step 9: Cleanup!** Please rinse all glassware and equipment prior to leaving lab. Return cleaned centrifuge tubes to the container without masking tape. Get a stamp in your lab notebook before leaving.
The typed lab report for the Qualitative Analysis of Group III Cations lab should be relatively short.

Make sure you include your unknown number or letter in the Conclusion (i.e. state something like "Unknown X had chromium and iron, but no aluminum or nickel.")

Include a flowchart for this week's lab as well as answers to the following postlab questions (most of which can be found on the first page of this lab, hint, hint 😊).

Postlab Questions:

1. Write balanced net ionic equations for the following reactions:
   a) Dissolving Fe(OH)₃ in nitric acid
   b) Oxidation of Cr(III) by hypochlorite ion in base.
   c) The confirmatory test for Ni²⁺.
   d) The confirmatory test for Fe³⁺.

2. A solution may contain any of the group III cations. Treatment of the solution with hypochlorite in an alkaline medium yields a yellow solution and a colored precipitate. The acidified solution is unaffected by treatment with NH₃. The colored precipitate dissolves in nitric acid; addition of excess NH₃ to this acid solution produces only a blue solution. On the basis of this information, which group III cations are present, absent or still in doubt? Explain. If still in doubt, how could you confirm or disprove its presence?