EXPERIMENT 16-17

Qualitative Analysis of Group III Cations

INTRODUCTION TO THE GROUP III CATIONS

The cations of group III: aluminum, iron (II), iron (III), nickel (II), cobalt (II), zinc, chromium (III) and manganese (II), are precipitated as hydroxides or sulfides from an aqueous solution buffered with ammonia and ammonium chloride and saturated with hydrogen sulfide. Under the buffered conditions, cations of later groups remain in solution. In this experiment we will deal with only four of the group III cations: iron (III), nickel (II), cobalt (II), and zinc.

\[
\begin{align*}
\text{Fe}^{3+} (aq) + 3\text{OH}^- (aq) & \rightarrow \text{Fe(OH)}_3 (s, \text{red}) \\
\text{Ni}^{2+} (aq) + \text{S}^2- (aq) & \rightarrow \text{NiS} (s, \text{black}) \\
\text{Co}^{2+} (aq) + \text{S}^2- (aq) & \rightarrow \text{CoS} (s, \text{black}) \\
\text{Zn}^{2+} (aq) + \text{S}^2- (aq) & \rightarrow \text{ZnS} (s, \text{white})
\end{align*}
\]

The group III cation’s precipitates do dissolve in a mixture of fairly concentrated hydrochloric and nitric acid. When these two acids are combined in the concentrated form, they are referred to as **aqua regia**. This mixture will dissolve any metal, and is one of the few solvents that will dissolve gold or platinum (the nitric acid oxidizes the metal atoms to ions, which form stable complex ions with chloride).

\[
\begin{align*}
\text{Fe(OH)}_3 (s) + 3\text{H}^+ (aq) & \rightarrow \text{Fe}^{3+} (aq, \text{yellow}) + 3\text{H}_2\text{O} (l) \\
\text{NiS} (s) + 2\text{H}^+ (aq) & \rightarrow \text{Ni}^{2+} (aq, \text{green}) + \text{H}_2\text{S} (g) \\
\text{CoS} (s) + 2\text{H}^+ (aq) & \rightarrow \text{Co}^{2+} (aq, \text{pink to blue}) + \text{H}_2\text{S} (g) \\
\text{ZnS} (s) + 2\text{H}^+ (aq) & \rightarrow \text{Zn}^{2+} (aq, \text{colorless}) + \text{H}_2\text{S} (g)
\end{align*}
\]

Hot concentrated nitric acid rids the solution of excess hydrogen sulfide by oxidation of the sulfide ion to sulfur.

\[
3\text{H}_2\text{S} (g) + 2\text{H}^+ (aq) + 2\text{NO}_3^- (aq) \rightarrow 2\text{NO} (g) + 3\text{S} (s) + 4\text{H}_2\text{O} (l)
\]

The addition of a strong base separates the iron (III), cobalt (II), and nickel (II) ions from the zinc ions. The first three form gelatinous hydroxide precipitates, while the zinc, being amphoteric, redissolves in excess strong base forming the zincate ion.

\[
\begin{align*}
\text{Fe}^{3+} (aq) + 3\text{OH}^- (aq) & \rightarrow \text{Fe(OH)}_3 (s, \text{red}) \\
\text{Ni}^{2+} (aq) + 2\text{OH}^- (aq) & \rightarrow \text{Ni(OH)}_2 (s, \text{green}) \\
\text{Co}^{2+} (aq) + 2\text{OH}^- (aq) & \rightarrow \text{Co(OH)}_2 (s, \text{blue}) \\
\text{Zn}^{2+} (aq) + 4\text{OH}^- (aq) & \rightarrow \text{Zn(OH)}_4^{2-} (aq, \text{colorless})
\end{align*}
\]
1. **IRON (III) ION.** The gelatinous hydroxide precipitates of iron (III), nickel (II), and cobalt (II) dissolve in sulfuric acid and hydrogen peroxide. The cobalt (II) can carry any color ranging from wine red to pink to blue. When the dissolved precipitates are treated with potassium thiocyanate, a blood red solution is produced due to the iron (III) complexing with the thiocyanate ion, which is very stable in aqueous solution.

\[
\text{Fe}^{3+}(aq) + \text{SCN}^{-}(aq) \rightarrow \text{FeSCN}^{2+}(aq, \text{blood red})
\]

This confirms the presence of iron (III) ions.

2. **COBALT (II) ION.** Cobalt (II) also forms a complex with thiocyanate ion, but it is only stable in alcoholic solution. The aqueous solution of the dissolved precipitates is saturated with fluoride ions, which tie up all of the iron (III) ions as a colorless hexafluoroferrate (III) ions. Ethyl alcohol (ethanol) is then added to the solution, along with ammonium thiocyanate, to produce the sky blue complex.

\[
\text{Co}^{2+}(aq) + 4\text{SCN}^{-}(aq) \rightarrow \text{Co(SCN)}_4^{2-}(aq, \text{sky blue})
\]

The sky blue color confirms the presence of cobalt (II) ions.

3. **NICKEL (II) ION.** The solution of the dissolved precipitates is made basic with ammonia to precipitate any iron (III) as iron (III) hydroxide and to form the soluble hexaamminenickel (II) complex. To the clear supernatant that remains, dimethyl glyoxime (DMG) is added, which forms a strawberry red precipitate with nickel (II) ions.

\[
2\text{(CH}_3\text{)}_2\text{C}_2\text{(NOH)}_2(aq) + \text{Ni(NH}_3)_6^{2+}(aq, \text{light blue}) \rightarrow 2\text{NH}_4^+(aq) + 4\text{NH}_3(aq) + \text{NiC}_9\text{H}_{14}\text{N}_4\text{O}_4(s, \text{strawberry red})
\]

The strawberry red precipitate confirms the presence of nickel (II) ions.

4. **ZINC ION.** Acidifying a solution containing the zincate ion will produce zinc ions.

\[
\text{Zn(OH)}_4^{2-}(aq) + 4\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + 4\text{H}_2\text{O(l)}
\]

The addition of potassium hexacyanoferrate (II) to the acidic solution of zinc ions produces a grayish-white to bluish-green precipitate.

\[
2\text{K}^+(aq) + 3\text{Zn}^{2+}(aq) + 2\text{Fe(CN)}_6^{4-}(aq) \rightarrow \text{K}_2\text{Zn}_3[\text{Fe(CN)}_6]_2(s, \text{green})
\]

The colored precipitate confirms the presence of zinc ions.
PROCEDURE

0. Students will work individually for this experiment. Except for the laboratory handout, remove all books, purses, and such items from the laboratory bench top, and placed them in the storage area by the front door. For laboratory experiments you should be wearing closed-toe shoes. Tie back long hair, and do not wear long, dangling jewelry or clothes with loose and baggy sleeves. Open you lab locker. Put on your safety goggles, your lab coat, and gloves.

PART A – PREPARATION OF GROUP III CATIONS

0. Prepare a gently-boiling water bath in your fume hood by half-filling a 250-mL beaker with water, placing it on your hot plate, and adjusting it to a setting that will allow the water to just boil. From the Mike Trout Qual Wall, observe individual solutions of Fe$^{3+}$, Ni$^{2+}$, and Co$^{2+}$, Zn$^{2+}$, and record your observations in the Known Data Table. To analyze the sample solution on day one, take a 50-mL beaker to the stock bottle of sample solution (containing Fe$^{3+}$, Ni$^{2+}$, and Co$^{2+}$, Zn$^{2+}$), found on the cart. Dispense 5 mL of the sample solution into a 50-mL beaker using the pipet pump, and label it with your name and as sample. To analyze the unknown simultaneously, place 5 mL of the unknown solution into a second clean centrifuge tube, and label it with your name and as unknown. Observe the solution, and record your observations in the Unknown Data Table.

The following steps will be done to both solutions.

1. Boil the solutions gently on the hot plate until their volumes are reduced by half. Then, add 1 mL of 1 M ammonium chloride to each beaker, and swirl to dissolve any crystallized salts. Pour the solutions into a clean centrifuge tubes and then, while stirring, add 6 M ammonia until the solutions are just basic to litmus. When the solutions are just basic, add 10 additional drops to each.

Saturate the solutions with hydrogen sulfide by adding 1 mL of 1 M thioacetamide, then heat them in the boiling water bath for seven minutes. Obtain two capillary pipets, one for your known and one for your unknown. After the seven minutes, centrifuge, then with a capillary pipet carefully decant out as much of the supernatants (absolutely no traces of precipitate) into two different, clean centrifuge tubes. Save the precipitates for the group III analysis, and discard the supernatants, cleaning the centrifuge tubes they were in for use later.
PART B – SEPARATION OF GROUP III CATIONS

2. Wash the precipitates from step 1 twice each with a mixture of 1 mL of ammonium chloride and 2 mL of water, and discard the washing.

   **CAUTION:** Wear gloves and use caution with the concentrated acids as they are skin irritants. Do not let them contact your skin.

   To each add 10 drops of 12 M hydrochloric acid, 10 drops of 6 M nitric acid and mix thoroughly. Pour the slurries into a two different, clean 50 mL beaker and boil the liquids gently on the hot plate for about one minute. **Do not heat to dryness.**

   **CAUTION:** If your hot plate is too hot, the liquids will splatter.

   Add 1 mL of cold water, mix to each, and decant the solutions into two different, clean centrifuge tubes with capillary pipets, discarding any solid free sulfur. If there are floating particles, suck up the solution from the middle with the capillary pipets.

3. Add drops of 6 M sodium hydroxide to each, mixing after each drop to make sure the solutions are homogeneous, until the solutions are basic to litmus, then add 15 more drops of sodium hydroxide. If the quantity of precipitate is so large that the product is mushy or nonfluid, add 10 to 20 drops of water. Centrifuge and decant the supernatants, and save the **supernatants** for step 8.

4. To the precipitates from step 3, add 2 mL of 3 M sulfuric acid and mix thoroughly. Add 1 mL of 3% hydrogen peroxide, and place the centrifuge tubes in the hot water bath for 1 minute. The precipitates should readily dissolve upon stirring. If they do not, repeat the addition of the sulfuric acid and hydrogen peroxide, and heat again for another minute. Once the precipitates have dissolved, add 10 drops of water, allow to cool, note the color of the solutions, and divide each solution into three approximately equal portions in clean, 100 mm glass test tubes.

PART C – TEST FOR IRON (III) IONS

5. To one of the three equal portions prepared in step 4, add 1 or 2 drops of 1.0 M potassium thiocyanate. A blood red solution proves the presence of iron.

PART D – TEST FOR COBALT (II) IONS

6. To another one of the three equal portions prepared in step 4, add a spatulaful of solid sodium fluoride to form a saturated solution, mixing well by stirring. A **saturated solution will have a significant amount of undissolved, white sodium fluoride at the bottom of the test tube after thorough mixing.** Add 10-20 drops of a saturated solution of ammonium thiocyanate in ethyl alcohol. The formation of a blue solution proves the presence of cobalt.

PART E – TEST FOR NICKEL (II) IONS

7. To the final one of the three equal portions prepared in step 4, add 6 M ammonia, shaking or stirring after each drop, until basic to litmus. If a precipitate forms, centrifuge and decant, and discard the solid. Clear the supernatant by adding 2-4 drops of dimethyl glyoxime. Mix thoroughly, and allow to stand for 1 minute. A strawberry-red precipitate proves the presence of nickel.
PART F – TEST FOR ZINC IONS

8. Add 6 M hydrochloric acid to the supernatants from step 3, mixing after each drop, until the solution is acidic to litmus. Then add 3 drops of 0.2 M potassium ferrocyanide to each and stir. A grayish-white to bluish-green precipitate confirms the presence of zinc. Centrifuge to make the precipitate more compact for examination.

11. Identify the cations present in your unknown and record them at the top of your Data Table.

12. All excess solutions (including any remaining unknown solution) should be disposed of in the Chem 1B Waste Container in the fume hood. Return the unknown test tube to the front counter.

13. Clean and wipe dry your laboratory work area and all apparatus. When you have completed your lab report have the instructor inspect your working area. Once your working area has been checked your lab report can then be turned in to the instructor.
The following is a flow chart for the separation and identification of the Group III cations.

\[ \text{Fe}^{3+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{and the cations of Groups IV, V} \]

\[ [(1) 1 \text{ M NH}_4\text{Cl}, 6 \text{ M NH}_3, 1 \text{ M thioacetamide}] \]

- white to red to black solid (Fe(OH)$_3$, CoS, NiS, ZnS)
  - save for Group IV separation or discard
  - [2 M HCl, 6 M HNO$_3$]

- yellow-black solid (S$_8$)
  - discard

- colorless or colored solution (Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$)
  - [3 M NaOH]

- colored solid (Fe(OH)$_3$, Co(OH)$_2$, Ni(OH)$_2$)
  - [4 M H$_2$SO$_4$, 3% H$_2$O$_2$]
  - [5 M KSCN]

  - blood red solution (Fe(SCN)$^{3-}$)
    - Fe$^{3+}$

  - sky blue solution (Co(SCN)$_2$$^{2-}$)
    - Co$^{2+}$

  - strawberry red solid (NiC$_4$H$_7$N$_2$O$_3$)
    - Ni$^{2+}$

- colorless solution (Zn(OH)$_4$$^{2-}$)
  - [6 M HCl]
  - [7 M NH$_3$, dimethyl glyoxime]
  - [8 M NaF, NH$_4$SCN in EtOH]

  - green solid (K$_2$Zn$_3$[Fe(CN)$_6$])
    - Zn$^{2+}$
# EXPERIMENT 16-17 LAB REPORT

Name: ___________________________________________  Student Lab Score: ________________
Date/Lab Start Time: _____________________________  Lab Station Number: ________________

## KNOWN DATA TABLE

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# UNKNOWN DATA TABLE

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QUESTIONS

1. Give the color of each of the following ions in solution:

(a) \( \text{Cu}^{2+} \) __________________
(b) \( \text{Co}^{2+} \) __________________
(c) \( \text{Ni}^{2+} \) ________________
(d) \( \text{Fe}^{3+} \) ________________
(e) \( \text{Fe}^{2+} \) ________________
(f) \( \text{Zn}^{2+} \) ________________
(g) \( \text{Cu(NH}_3)_4^{2+} \) ________________
(h) \( \text{FeSCN}^{2+} \) ________________
(i) \( \text{Co(SCN)}_4^{2-} \) ________________
(j) \( \text{CrO}_4^{2-} \) ________________
(k) \( \text{Cr}_2\text{O}_7^{2-} \) ________________
(l) \( \text{MnO}_4^- \) ________________

2. If no precipitate forms in step 1, what can you conclude?

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

3. Why can zinc ions be separated from iron (III), cobalt (II), and nickel (II) ions by the addition of excess sodium hydroxide? Indicate the reactions that occur.

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

reaction: __________________________________________________________________

reaction: __________________________________________________________________

reaction: __________________________________________________________________

reaction: __________________________________________________________________

4. Identify a reagent or reagents from the Group I, II, or III qualitative labs that would do the following:

(a) precipitate mercury (I) ions but not nickel (II) ions ________________

(b) precipitate copper (II) ions but not iron (III) ions ________________

(c) precipitate cobalt (II) ions but not zinc ions ________________
5. A solution contains only these ions: silver, lead (II), bismuth (III), antimony (III), nickel (II), and zinc. Prepare a flow chart to show how you would separate and identify the six ions in this solution.