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 five of the group III cations: aluminum, iron (III), nickel (II), cobalt (II), and zinc.

\[
\text{Al}^{3+} (aq) + 3\text{OH}^- (aq) \rightarrow \text{Al(OH)}_3 (s, \text{white})
\]

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

\[
\text{Ni}^{2+} (aq) + \text{S}^2^- (aq) \rightarrow \text{NiS} (s, \text{black})
\]

\[
\text{Co}^{2+} (aq) + \text{S}^2^- (aq) \rightarrow \text{CoS} (s, \text{black})
\]

\[
\text{Zn}^{2+} (aq) + \text{S}^2^- (aq) \rightarrow \text{ZnS} (s, \text{white})
\]

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).

\[
\text{Al(OH)}_3 (s) + 3\text{H}^+ (aq) \rightarrow \text{Al}^{3+} (aq, \text{colorless}) + 3\text{H}_2\text{O} (l)
\]

\[
\text{Fe(OH)}_3 (s) + 3\text{H}^+ (aq) \rightarrow \text{Fe}^{3+} (aq, \text{yellow}) + 3\text{H}_2\text{O} (l)
\]

\[
\text{NiS} (s) + 2\text{H}^+ (aq) \rightarrow \text{Ni}^{2+} (aq, \text{green}) + \text{H}_2\text{S} (g)
\]

\[
\text{CoS} (s) + 2\text{H}^+ (aq) \rightarrow \text{Co}^{2+} (aq, \text{pink to blue}) + \text{H}_2\text{S} (g)
\]

\[
\text{ZnS} (s) + 2\text{H}^+ (aq) \rightarrow \text{Zn}^{2+} (aq, \text{colorless}) + \text{H}_2\text{S} (g)
\]

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 and aluminum ions. The first three form gelatinous hydroxide precipitates, while the zinc and aluminum, being amphoteric, redissolve in excess strong base forming aluminate and zincate ions.

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

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

\[
\text{Co}^{2+} (aq) + 2\text{OH}^- (aq) \rightarrow \text{Co(OH)}_2 (s, \text{pink to blue})
\]

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

\[
\text{Zn}^{2+} (aq) + 4\text{OH}^- (aq) \rightarrow \text{Zn(OH)}_4^{2-} (aq, \text{colorless})
\]
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.

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

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.

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

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.

\[
2(CH_3)_2C_2(NOH)_2 (aq) + Ni(NH_3)_6^{2+} (aq, \text{light blue}) \rightarrow 2NH_4^+ (aq) + 4NH_3 (aq) + NiC_8H_{14}N_4O_4 (s, \text{strawberry red})
\]

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

4. **ALUMINUM ION**. Acidifying a solution containing the aluminate ion and the zincate ion, and then adding ammonia will precipitate the aluminum as aluminum hydroxide, but the zinc ion forms the soluble tetraamminezinc complex.

\[
\begin{align*}
Al(OH)^- (aq) + 4H^+ (aq) & \rightarrow Al^{3+} (aq) + 4H_2O (l) \\
Zn(OH)_2^{2-} (aq) + 4H^+ (aq) & \rightarrow Zn^{2+} (aq) + 4H_2O (l) \\
Al^{3+} (aq) + 3NH_3 (aq) + 3H_2O (l) & \rightarrow Al(OH)_3 (s) + 3NH_4^+ (aq) \\
Zn^{2+} (aq) + 4NH_3 (aq) & \rightarrow Zn(NH_3)_4^{2+} (aq)
\end{align*}
\]

The precipitate is dissolved in acetic acid, then catechol violet reagent (1,2-dihydroxybenzene) is added, forming a complex with aluminum ions.

\[
\begin{align*}
Al(OH)_3 (s) + 3C_6H_4(OH)_2 & \rightarrow Al(C_6H_4O_2)_3^{5-} (blue) + 3H_2O (l)
\end{align*}
\]

A blue solution confirms the presence of aluminum ions.

5. **ZINC ION**. The addition of potassium hexacyanoferrate (II) to an acidic solution of zinc ions produces a grayish-white to bluish-green precipitate.

\[
\begin{align*}
Zn(NH_3)_5^{2+} (aq) + 4H^+ (aq) & \rightarrow Zn^{2+} (aq) + 4NH_4^+ (aq) \\
2K^+ (aq) + 3Zn^{2+} (aq) + 2Fe(CN)_6^{4-} (aq) & \rightarrow K_2Zn[Fe(CN)_6]_2 (s, \text{green})
\end{align*}
\]

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 your lab locker. Put on your safety goggles, your lab coat, and gloves.

0. Your instructor will indicate how you will perform the qualitative analysis. You will either (1) use the first lab period (day one) to conduct the analysis on the known sample and then the second lab period (day two) to conduct the analysis on the unknown sample, or (2) use two full lab periods to analyze the known sample and the unknown sample simultaneously. Make sure to paste the unknown code label on your flow chart in the space provided.

PART A – PREPARATION OF GROUP III CATIONS

0. From the Qual Wall, observe individual solutions of Al$^{3+}$, Fe$^{3+}$, Ni$^{2+}$, and Co$^{2+}$, Zn$^{2+}$, and record your observations in the flow chart. To analyze the sample solution on day one, take a 50-mL beaker to the stock bottle of sample solution (containing Al$^{3+}$, Fe$^{3+}$, Ni$^{2+}$, and Co$^{2+}$, Zn$^{2+}$), found on the balance table. 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. On day two, or, if you are analyzing the known and unknown samples simultaneously, you will place 5 mL of your unknown sample in a 50 mL beaker, and label it with your name and as unknown.

Boil the solution gently on the hot plate until the volume is reduced by half.

1. Add 1 mL of 1 M ammonium chloride to the beaker, and swirl to dissolve any crystallized salts. Pour the solution into a clean centrifuge tube and then, while stirring, add 6 M ammonia until the solution is just basic to litmus. When the solution is just basic, add 10 additional drops.

Saturate the solution with hydrogen sulfide by adding 1 mL of 1 M thioacetamide, then heat in a 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 supernatant (absolutely no traces of precipitate) into a clean centrifuge tube. Save the precipitate for the group III analysis.

If you are not testing for Group IV and V cations today, discard the supernatant and continue on with step 2. If you will be testing for Group IV and V cations today, add a few drops of 1 M thioacetamide to the supernatant and return it to the boiling water bath for a few minutes more to check for complete precipitation of the Group III cations. Any precipitate formed may be discarded.
PART B – SEPARATION OF GROUP III CATIONS

2. Wash the precipitate from step 1 twice 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.

   Add 10 drops of 12 M hydrochloric acid, 10 drops of 6 M nitric acid and mix thoroughly. Pour the slurry into a clean 50 mL beaker and boil the liquid 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, and decant the solution into a clean centrifuge tube with a capillary pipet, discarding any solid free sulfur. If there are floating particles, suck up the solution from the middle with the capillary pipet.

3. Add drops of 6 M sodium hydroxide, mixing after each drop to make sure the solution is homogeneous, until the solution is 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 supernatant, and save the supernatant for step 8.

4. To the precipitate 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 tube in the hot water bath for 1 minute. The precipitate should readily dissolve upon stirring. If it does not, repeat the addition of the sulfuric acid and hydrogen peroxide, and heat again for another minute. Once the precipitate has dissolved, add 10 drops of water, allow to cool, note the color of the solution, and divide it 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 ALUMINUM IONS

8. To the supernatant from step 3, add 6 M acetic acid slowly with mixing until acidic to litmus. If the solution is more than 2 mL, transfer to a 50 mL beaker and boil down to about 2 mL. Pour the solution back into a clean, glass test tube, add drops of 6 M ammonia, mixing after each drop, until the solution is basic to litmus, and then add 10 more drops. A translucent, gelatinous precipitate is indicative of aluminum hydroxide, but because the precipitate is highly translucent, very finely divided, and the color of opaque, bluish-white glass, it is not easy to detect. Use a dark piece of paper to help you see the featherlike precipitate. Transfer to a centrifuge tube and centrifuge the solid to the bottom of the tubes for step 9, and decant the supernatant into a clean centrifuge tube and save for step 10.

9. To confirm for aluminum, wash the precipitate twice with 2 mL of hot water and discard the washings. Dissolve the precipitate with 2 drops of 6 M acetic acid. Do not add more than 2 drops. Stir to get it to dissolve. Add 3 mL of water and 2 drops of catechol violet reagent and stir. A blue solution proves the presence of aluminum.

PART G – TEST FOR ZINC IONS

10. Add 6 M hydrochloric acid to the supernatant from step 8, mixing after each drop, until the solution is acidic to litmus. Then add 3 drops of 0.2 M potassium ferrocyanide 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: Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Al$^{3+}$, Zn$^{2+}$, and the cations of Groups IV, V

1. (1) 1 M NH$_4$Cl, 6 M NH$_3$, 1 M thioacetamide
   - black solid (Fe(OH)$_3$, CoS, NiS, Al(OH)$_3$, ZnS)
   - solution (Groups IV, V)
     - [2] 12 M HCl, 6 M HNO$_3$
     - save for Group IV separation or discard
   - yellow-black solid (S$_4$)
   - discard

2. (3) 6 M NaOH
   - brown solid (Fe(OH)$_3$, Co(OH)$_2$, Ni(OH)$_2$)
   - colorless solution (Al(OH)$_4^-$, Zn(OH)$_4^{2-}$)
     - [4] 3 M H$_2$SO$_4$, 3% H$_2$O$_2$
     - colored solution (Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$)
     - [5] 1 M KSCN
     - [6] NaF, NH$_4$SCN in EtOH
     - [7] 6 M NH$_3$, dimethyl glyoxime
     - blood red solution (Fe(SCN)$^{3-}$)
     - sky blue solution (Co(SCN)$_2^{3-}$)
     - strawberry red solid (NiC$_8$H$_4$N$_2$O$_4$)
   - [8] 6 M HC$_2$H$_3$O$_2$, 6 M NH$_3$
     - white solid (Al(OH)$_3$)
     - colorless solution (Zn(NH$_3$)$_4^{2-}$)
     - [9] 6 M HC$_2$H$_3$O$_2$, catechol
     - blue solution (Al(C$_6$H$_5$O$_2$)$_2^{3-}$)
     - [10] 6 M HCl, 0.2 M K$_2$Fe(CN)$_6$
     - green solid (K$_2$Zn$_2$[Fe(CN)$_6$]$_2$

Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Al$^{3+}$, Zn$^{2+}$
**EXPRESSMENT 16-17 LAB REPORT**

Name: ___________________________________________ Student Lab Score: ____________

Date/Lab Start Time: _____________________________ Lab Station Number: ________________

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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) $\text{Fe}^{3+}$
(f) $\text{Cu(NH}_3\text{)}_4^{2+}$
(g) $\text{Zn(NH}_3\text{)}_4^{2+}$
(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 aluminum and 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.

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

4. Why can aluminum ions be separated from zinc ions by the addition of aqueous ammonia? Indicate the reactions that occur.

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

5. 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 aluminum ions

________________________________________________________________________
6. 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.