

CATION GROUP III – PART II

ANALYTICAL PROCEDURES FOR CATION GROUP III

Safety:

NICKEL (II) NITRATE Harmful if swallowed or inhaled. Causes irritation to skin, eyes, and respiratory tract. May cause allergic skin or respiratory reaction. Can cause cancer.

COBALT (II) NITRATE May cause allergic respiratory reaction. May cause allergic skin reaction. May be harmful if swallowed. May cause cardiac disturbances. Causes eye and skin irritation. Causes digestive and respiratory tract irritation. May cause blood abnormalities

POTASSIUM CHROMATE May cause allergic respiratory reaction. Corrosive. Causes eye and skin burns. Causes digestive and respiratory tract burns. May cause cancer in humans

Disposal:

All mixtures must be disposed in the waste container labeled: Cation Group III Waste Container with the exception of the Cobalt mixture which goes into the waste container labeled: Waste $\text{Co}(\text{SCN})_2[\text{O}=\text{C}(\text{CH}_3)_2]_2$

The following procedures are to be used for analyzing both known and unknown solutions.

PROCEDURE I: Sample Preparation

Preparation of Known Sample: In a (labeled) 50 mL beaker mix 6 drops of each test solution of the Cation III ions: Fe^{3+} , Al^{3+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} , Cr^{3+} .

Preparation of Unknown Sample: Place **Approximately 1 mL** of the unknown solution in a (labeled) 50 mL beaker. This is the sample you will analyze. Store the remainder of the unknown solution. The unknown sample and known sample will be analyzed simultaneously.

NOTES: When centrifuging, don't forget to COUNTERBALANCE sample.

Always MIX WELL after addition of a reagent to sample.

To wash a precipitate: add about 15 drops of hot DI water. Stir well. Centrifuge and discard supernatant.

PROCEDURE II: Precipitation and Separation of Subgroups of Group III

- A. **Separation of Aluminum Subgroup** - (Cr, Al, and Zn) From Rest of Group III: To your sample, add 6 M NaOH solution until solution is basic to universal pH paper, then add 8 drops excess. Add 15-18 drops of **fresh** 3% H_2O_2 slowly, stir for 1 min. Carefully heat the solution until it is just boiling and boil for 2 minute, replenishing the water lost. Remove from heat and transfer to a 4 inch test tube.

Centrifuge

PRECIPITATE: $\text{Fe}(\text{OH})_3$, MnO_2 , $\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_3$

- B. **Separation of Iron Subgroup** - (Fe & Mn) from Nickel Subgroup (Ni & Co): Wash precipitate (see above note) three times with hot DI water and discard the washings. To the precipitate add 10 drops of 6 M HCl and 4 drops of 6 M HNO_3 . Add 8 drops conc. HCl and 8 drops conc. HNO_3 . **MIX WELL**. Heat until the precipitate dissolves as much as possible. Add concentrated aqueous NH_3 dropwise until the solution is basic, and then add 1 drop of concentrated aqueous NH_3 solution in excess.

Centrifuge

SUPERNATANT:

$\text{Al}(\text{OH})_4^-$, CrO_4^{2-} , $\text{Zn}(\text{OH})_4^{2-}$

Stopper and label. Treat according to Procedure V.

PRECIPITATE: $\text{Fe}(\text{OH})_3$, MnO_2

Stopper and label. Treat according to Procedure IV.

SUPERNATANT: $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Ni}(\text{NH}_3)_6^{2+}$

Stopper and label. Treat according to Procedure III.

PROCEDURE III: Analysis of Nickel Subgroup

SUPERNATANT: $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Ni}(\text{NH}_3)_6^{2+}$
(from Procedure II, part B)

A. Treatment of the $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Ni}(\text{NH}_3)_6^{2+}$ Supernatant from Procedure II, part B: Divide the solution into two separate equal portions.

1/2

1/2

One-half (1/2) of the Supernatant

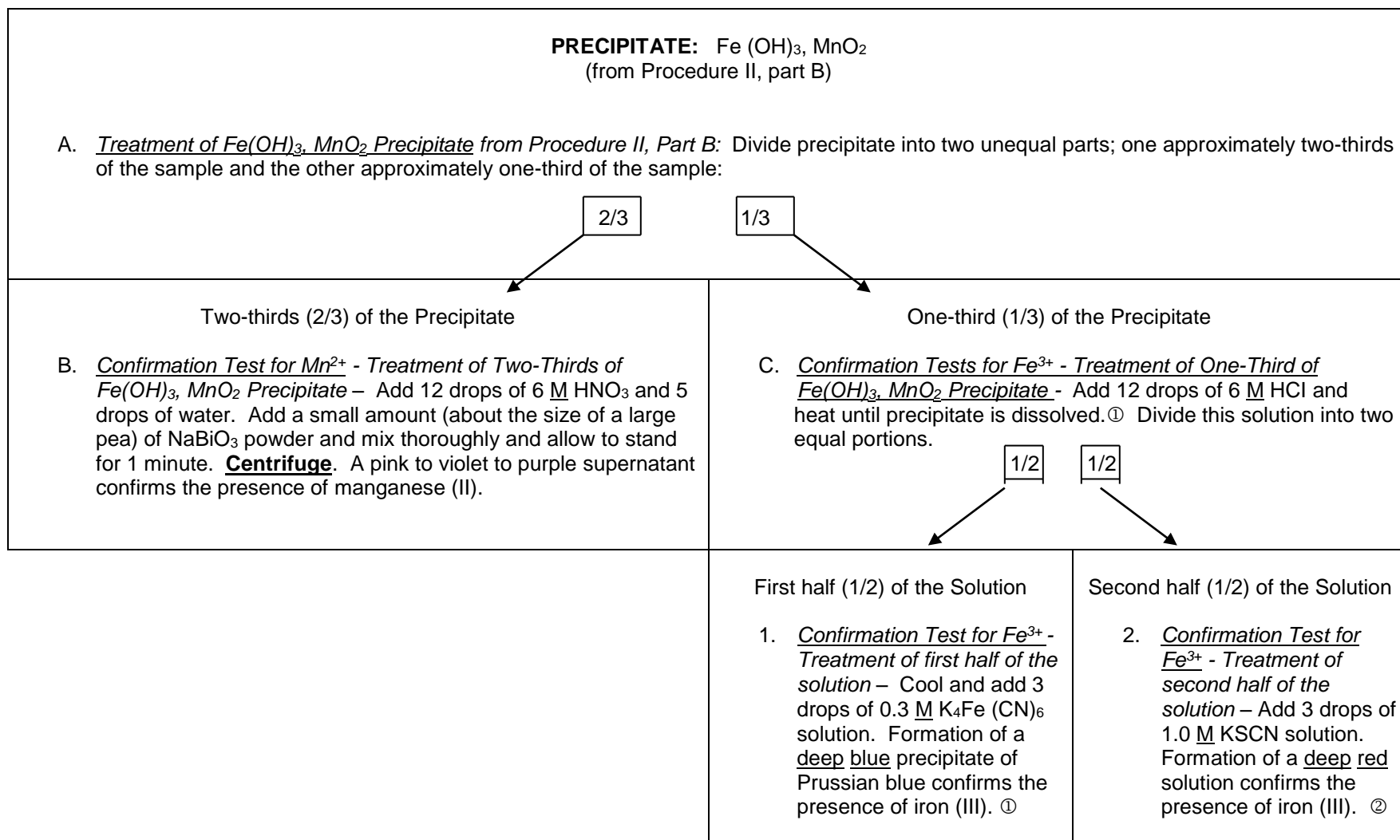
B. Confirmation Test for Co^{3+} - Treatment of One-Half of $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Ni}(\text{NH}_3)_6^{2+}$ Solution – Add 6 M acetic acid until acidic, then 10 drops of 1.0 M KSCN solution. Then carefully, without mixing, add 1 mL of acetone into the test tube to form a layer on top. The formation of a sky blue color in the acetone layer confirms the presence of cobalt (II).^①

One-half (1/2) of the Supernatant

C. Confirmation Test for Ni^{2+} - Treatment of One-Half of $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Ni}(\text{NH}_3)_6^{2+}$ Solution – Add 6 drops of 1.5% dimethylglyoxime, $(\text{CH}_3)_2\text{C}_2(\text{NOH})_2$, and 2 drops of concentrated aqueous NH_3 . Formation of a strawberry-red precipitate confirms the presence of nickel (II).

^① The formula for the blue coordination compound is $\{\text{Co}(\text{SCN})_3[\text{O}=\text{C}(\text{CH}_3)_2]_3\}$.

PROCEDURE IV: Analysis of Iron Subgroup



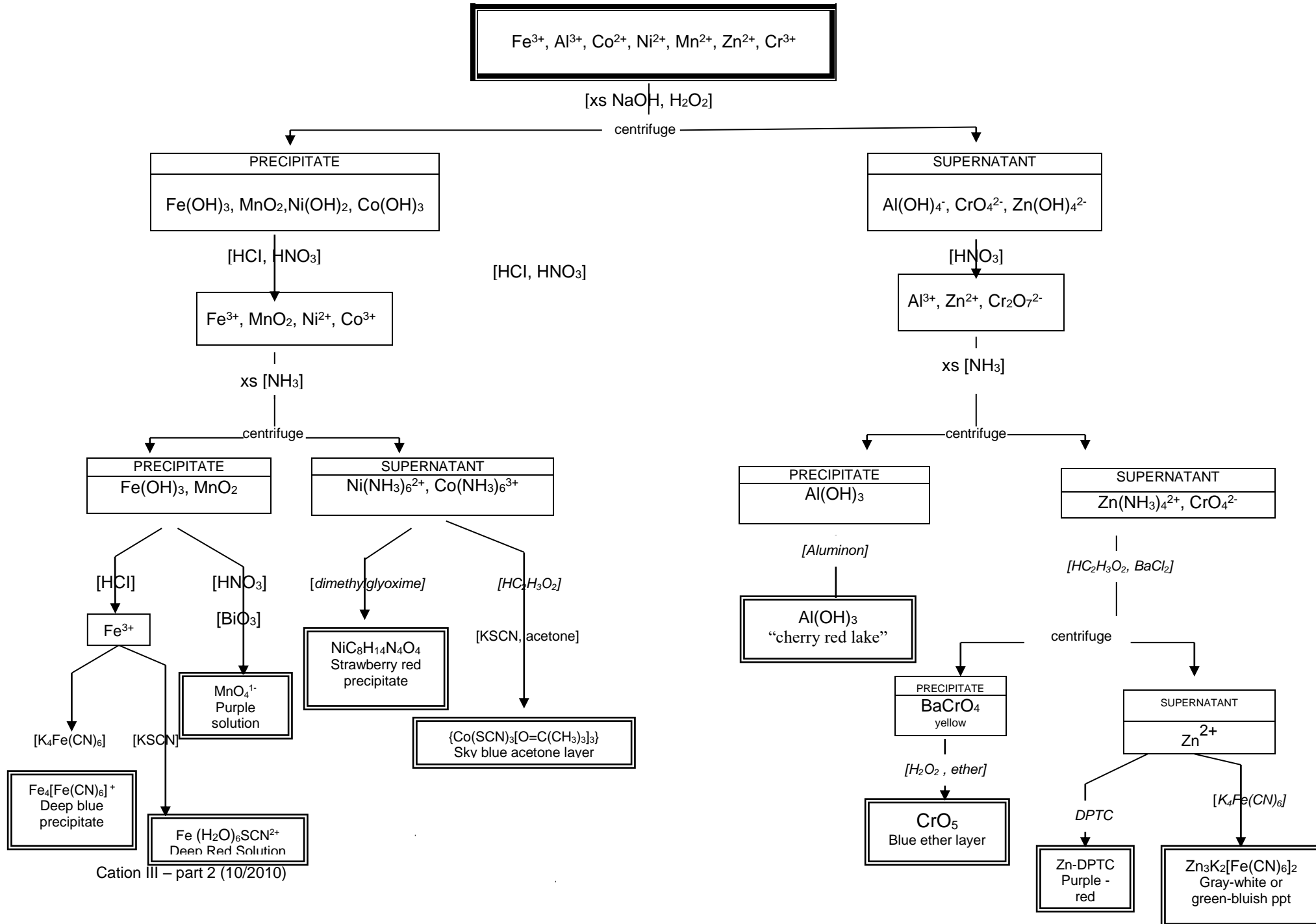
- ① A faint blue colored precipitate (not a dark blue precipitate) formed when testing your unknown sample is probably due to a trace of iron or the presence of some other metallic ion which has not been completely removed. If the test does not give a deep dark blue precipitate, iron (III) may be assumed to be absent.
- ② If the solution is a deep red, iron (III) should be reported present in your unknown.

PROCEDURE V: Analysis of Aluminum Subgroup

<p>SUPERNATANT: Al(OH)_4^-, CrO_4^{2-}, Zn(OH)_4^{2-} (from Procedure II, part A)</p> <p><i>Treatment of Al(OH)_4^-, CrO_4^{2-}, Zn(OH)_4^{2-} Supernatant from Procedure II, part A – Separation of Al from Cr and Zn, and Confirmation Test for Al^{3+}:</i> Add conc HNO_3 until the solution is just acidic; then add concentrated aqueous NH_3 dropwise until the solution is basic, and then add 3 drops of concentrated aqueous NH_3 in excess. Stir for 1 minute. Heat for 5 minutes in a hot water bath. Formation of a white flocculent gelatinous precipitate confirms the presence of aluminum. Centrifuge.</p>	
<p>PRECIPITATE: Al(OH)_3</p> <p>B. <u>Confirmation test for Al^{3+}</u> Wash the precipitate two times with hot water. Add 2-3 drops of 6 M HNO_3 to dissolve the precipitate. Add 2 drops of aluminon, mix, and add 6 M NH_3 until slightly basic. Mix thoroughly. Centrifuge. A cherry red precipitate called a “lake” of Al(OH)_3 and absorbed aluminon dye confirms the presence of aluminum. ①</p>	<p>SUPERNATANT: CrO_4^{2-}, $\text{Zn(NH}_3)_4^{2+}$</p> <p>C. <u>Separation of Cr and Zn⁺</u>: If the solution is yellow, the presence of chromium (III) is probable. ② Acidify the solution with 6 M acetic acid. If the supernatant is greater than 1 mL, transfer the supernatant to a beaker and evaporate to approx. 1 mL and then transfer the supernatant back to the 4 inch test tube. Add a small amount (about the size of a pea) of $\text{NaC}_2\text{H}_3\text{O}_2$, and then 5 drops or enough 120 g/L BaCl_2 solution so that precipitation is complete. ③ Centrifuge. ④</p>
<p>PRECIPITATE: BaCrO_4</p> <p>D. <u>Confirmation Test for Cr^{3+}</u> - Wash the precipitate two times with hot DI water and discard the washings. Add 2 drop of 6 M HNO_3, heat gently and stir for about 1 min; Add 10 drops of DI water. Mix and cool to RT. IN THE HOOD, add 10 drops of ether and 1 drop of 3% H_2O_2. Mix well. The formation of a blue color in the ether layer confirms the presence of chromium.</p>	<p>SUPERNATANT: Zn^{2+}</p> <p>D. <u>Confirmation tests for Zn^{2+}</u>: Divide the supernatant in $\frac{1}{2}$ ⑤</p> <p>Test 1. IN THE HOOD: To the the first $\frac{1}{2}$ of the supernatant add 3 drop of dithizone (phenylthiocarbazone). Wait for 1 minute. If a purple-red color forms, the presence of Zn is confirmed. .</p> <p>Test 2. With the remainder of the supernatant, add 6 M HCl until acidic, then add 3 drops of 0.3 M $\text{K}_4\text{Fe(CN)}_6$. Mix and centrifuge. A grayish white to green - bluish precipitate confirms the presence of Zn.</p>

- ① Al(OH)_3 is a gelatinous, flocculent, highly translucent, and the color of opaque, bluish white glass, and its presence is not easy to see. Therefore the dye, aluminon, is added to aid in the detection of the white flocculent precipitate of Al(OH)_3 . All Cr^{3+} must be oxidized to CrO_4^{2-} because Cr^{3+} is very similar in properties to Al^{3+} , and would precipitate on addition of aqueous NH_3 as Cr(OH)_3 , which is green. In small amounts the color may not be apparent, and as a result, Cr(OH)_3 may be mistaken for Al(OH)_3 .
- ② If CrO_4^{2-} is present, the supernatant from Procedure I, part A should be yellow. The yellow color is a sensitive test for CrO_4^{2-} , and if the supernatant from Procedure I, part A is colorless, assume that chromium (III) is absent.
- ③ Since BaCrO_4 can be very finely divided, it can appear very pale yellow and almost white. The confirmation test for Cr must be performed, even if the precipitate appears white.
- ④ If the supernatant is still yellow after centrifuging, the chromate ion has not all been precipitated as BaCrO_4 . Add more BaCl_2 to the supernatant to complete the precipitation and centrifuge again.
- ⑤ For the first test, the purple-red color is assumed to be the formation of a complex ion formed between Zn^{2+} and diphenylthiocarbazone molecules. In the second test, when 0.3 M $\text{K}_4\text{Fe(CN)}_6$ is added, the solution should remain acidic.

CATION GROUP III – THE ALUMINUM-NICKEL-IRON GROUP – FLOW CHART



SUPERNATANT

$\text{Al}(\text{OH})_4^-, \text{CrO}_4^{2-}, \text{Zn}(\text{OH})_4^{2-}$

|

[HNO₃]

$\text{Al}^{3+}, \text{Zn}^{2+}, \text{Cr}_2\text{O}_7^{2-}$

|

xs [NH₃]

centrifuge

PRECIPITATE

$\text{Al}(\text{OH})_3$

|

[Aluminon]

$\text{Al}(\text{OH})_3$
"cherry red lake"

SUPERNATANT

$\text{Zn}(\text{NH}_3)_4^{2+}, \text{CrO}_4^{2-}$

|

[HC₂H₃O₂, BaCl₂]

centrifuge

PRECIPITATE

BaCrO_4
yellow

|

[H₂O₂, ether]

CrO_5
Blue ether layer

SUPERNATANT

Zn^{2+}

|

DPTC

Zn-DPTC
Purple - red

[K₄Fe(CN)₆]

$\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$
Gray-white or green-bluish ppt

Cation III Separation Reactions:

