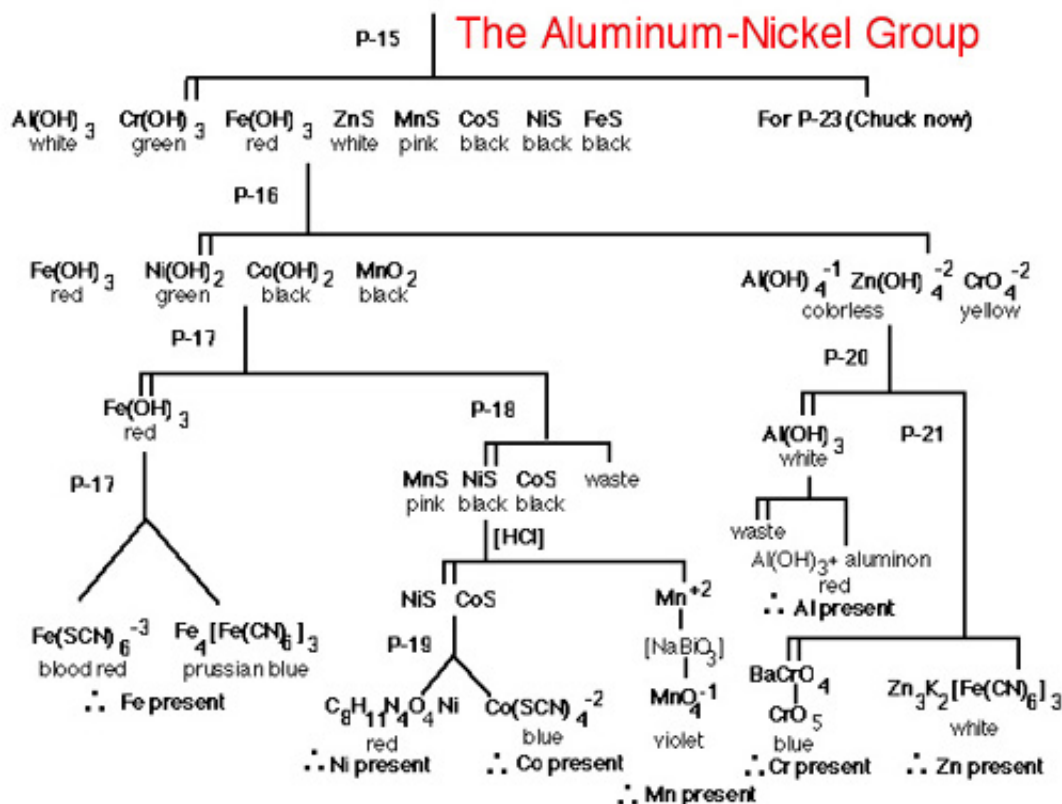


# The Aluminum Group



## Separation of the Aluminum Group from all others

**Facts:** Addition of  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{OH}$ , and  $(\text{NH}_4)_2\text{S}$  to a solution containing all the cations not precipitated in the preceding groups results in the precipitation of Aluminum, Chromium, and Iron(III) as hydroxides, and Manganese, Nickel, Cobalt, Iron(II), and Zinc as sulfides. Under these conditions the hydroxides and sulfides of Calcium, Barium, Magnesium, Potassium, and Sodium are soluble. This solubility permits a separation of the cations of the Aluminum-nickel group from those of the Barium-magnesium group.

## Procedure 15: Precipitation of the Aluminum group

If the solution to be analyzed is an Aluminum-nickel group "known" or "unknown", follow (A). If this is a Salt Analysis follow (B).

(A) Place 3 drops of the Aluminum group **known** [E-10] **OR unknown** [from instructor] in a test tube. [ **WARNING:** Never mix the **known** with the **unknown** ]. Add 4 drops of 2 M  $\text{NH}_4\text{Cl}$  [B-7], mix thoroughly, then add 15 M  $\text{NH}_4\text{OH}$  [A-8], drop by drop, with constant stirring until the solution is just alkaline (litmus test). Then add one extra drop, of 15 M  $\text{NH}_4\text{OH}$  [A-8] and 20 drops of hot water and mix thoroughly. Then add 8 drops of  $(\text{NH}_4)_2\text{S}$  [in hood] and mix thoroughly.

Heat the tube carefully for two minutes in the boiling water bath; avoid allowing the contents of the tube to overflow because of frothing.

Centrifuge, and test for complete precipitation with one a drop of  $(\text{NH}_4)_2\text{S}$  [hood]. When precipitation with  $(\text{NH}_4)_2\text{S}$  is complete, wash down the sides of the tube with a few drops of hot water, centrifuge, and decant, saving the decantate for Procedure 23. [If this is a salt analysis, save the decantate, which contains the cations of the groups that follow, for Procedure 23] (Chuck it for now).

Wash the precipitate three times with mixtures of of 10 drops of hot water plus 10 drops of 1 M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  [B-5], and analyze according to Procedure 16.

#### **If this is a Salt Analysis:**

**(B)** Place the decantate from Procedure 5 in a crucible and evaporate down carefully to a volume of about 10 drops. Transfer to a test tube, centrifuge, and decant into another test tube, discarding the precipitate. Treat the decantate in the test tube according to the directions beginning with the second sentence of Method **(A)**.

### **Separation of the Aluminum subgroup from the Nickel subgroup**

**Facts:** The hydroxides of Aluminum, Chromium, and Zinc are *amphoteric* and are therefore soluble in NaOH. In contrast, the hydroxides of Iron, Manganese, Cobalt, and Nickel are not *amphoteric*; they are not soluble in NaOH. Upon this fact is based the separation of the cations of the Aluminum subgroup ( $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Zn}^{2+}$ ) from the cations of the Nickel subgroup ( $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ ).

#### **Procedure 16: Separation of the Aluminum subgroup from the Nickel subgroup**

Treat the precipitate from Procedure 15 with 10 drops of 12 M HCl [hood], mix thoroughly, transfer to a crucible and simmer gently for half a minute. If the precipitate is not completely dissolved add 3 drops of 16 M  $\text{HNO}_3$  [hood] mix thoroughly and simmer until a clear solution is obtained (clear means that there is no **solid** present. It may be a *colored* solution).

Add 10 drops of cold water, transfer to a test tube, centrifuge to remove any precipitate of Sulfur, and decant into a crucible. Make the solution strongly alkaline (litmus test) with 8 M NaOH [hood] and mix thoroughly.

If the quantity of precipitate is so large that the product is mushy or nonfluid add 10 to 20 drops of water. Then add 2 drops of 3%  $\text{H}_2\text{O}_2$  [C-6], stir for one minute and then simmer for two minutes, replenishing the water lost. Transfer to a test tube before the precipitate has had a chance to settle, and centrifuge. Decant, saving the decantate for Procedure 20. Wash the precipitate three times with hot water and analyze according to Procedure 17.

### **Separation of iron from Manganese, Nickel, and Cobalt**

**Facts:** When  $\text{NH}_4\text{Cl}$  and excess  $\text{NH}_4\text{OH}$  are added to a solution containing Iron(III), Manganese, Nickel, and Cobalt ions, the Iron is precipitated as  $\text{Fe}(\text{OH})_3$  leaving  $\text{Mn}^{2+}$ ,  $\text{Ni}(\text{NH}_3)_6^{2+}$ , and  $\text{Co}(\text{NH}_3)_6^{2+}$  in solution.

### Procedure 17: Separation and detection of Iron

Treat the precipitate from Procedure 16 with 10 drops of 12 M HCl [hood], mix thoroughly, and heat carefully until completely dissolved. Add 10 drops of 2 M  $\text{NH}_4\text{Cl}$  [B-7], and then add 15 M  $\text{NH}_4\text{OH}$  [A-8], with constant stirring, until the solution is alkaline (litmus test).

Then add a 2 drop excess of 15 M  $\text{NH}_4\text{OH}$  [A-8]. Mix thoroughly, centrifuge at once, and decant immediately into a test tube, saving this decantate for Procedure 18.

Wash the precipitate three times with hot water; then dissolve it in 5 drops of 2 M HCl (A-3) and dilute with 10 drops of water. **Divide the solution into two parts.**

To one part add a drop of 0.2 M  $\text{K}_4\text{Fe}(\text{CN})_6$  [D-3]. A blue precipitate,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , (**Prussian Blue**) proves the presence of iron. **This test must be strong!**

To the second part add 0.2 M KSCN [D-6]. A red color, due to the *hexathiocyanatoferrate (III)* ion,  $\text{Fe}(\text{SCN})_6^{3-}$ , (**blood red**) proves the presence of iron. **This test must be strong!**

### Separation of Manganese from Cobalt and Nickel

**Facts:** Separation of Manganese from Cobalt and Nickel depends on the fact that when the sulfides of these three metals are treated with cold dilute HCl,  $\text{MnS}$  is dissolved immediately, whereas  $\text{CoS}$  and  $\text{NiS}$  are only very slightly affected.

### Procedure 18: Separation of Manganese from Cobalt and Nickel and detection of Manganese

Treat the decantate from Procedure 17 with 3 drops of  $(\text{NH}_4)_2\text{S}$  [hood]. Centrifuge and decant, discarding the decantate.

Wash the precipitate three times with hot water to which 5 drops of 2 M  $\text{NH}_4\text{Cl}$  [B-7] have been added. Add 10 drops of 2 M HCl [A-3] to this precipitate and stir for one minute.

Centrifuge, and draw off the supernatant liquid with a medicine dropper; save this decantate in a crucible for detection of manganese.

Wash the precipitate ( $\text{CoS}$ ,  $\text{NiS}$ ) once with 2 M HCl [A-3] and twice with hot water and save for Procedure 19.

**Detection of Manganese.** Boil the decantate, saved for the detection of Manganese, gently for about half a minute, cool, make just alkaline with 8 M NaOH [hood], and then add an excess of 1 drop of NaOH.

Transfer to a test tube, centrifuge and decant, discarding the decantate, and wash the precipitate three times with hot water. Treat this precipitate with 5 drops of 3 M  $\text{HNO}_3$  [A-6] and a few grains of solid Sodium bismuthate ( $\text{NaBiO}_3$ ) [D-9] (for re-fill, see the instructor). Mix thoroughly, allow to stand for one minute, then centrifuge. A pink to reddish-purple solution due to the presence of  $\text{MnO}_4^-$  proves the presence of Manganese.

### Procedure 19: Detection of Nickel and Cobalt

Treat the precipitate from Procedure 18 with 10 drops of 12 M HCl [hood] and 3 drops of 16 M HNO<sub>3</sub> [hood], mix thoroughly, and heat gently until a clear solution is obtained (remember that *clear* means that no solids are present. e.g. a *clear blue sky*).

Add 6 drops of water, mix well, centrifuge, and decant into a test tube, discarding the precipitate (**yellow Sulfur**). Make the decantate alkaline with 15 M NH<sub>4</sub>OH [A-8] and divide it into two parts.

To one part add 5 drops of Dimethyl glyoxime [C-3]. A **strawberry-red** precipitate (NiC<sub>8</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>) proves the presence of Nickel. Call this precipitate *Nickel Glyoxime*.

Make the second part acid with 2 M H<sub>2</sub>SO<sub>4</sub> [A-5]. Saturate with NaF [D-11] (for re-fill, see the instructor) by adding 5 mm of solid NaF on the end of a spatula. Stir for one minute. Then add 15 drops of a saturated solution of "Ammonium thiocyanate in alcohol" [C-1]. A **blue** solution, due to the *Tetrathiocyanatocobaltous II* ion, Co(SCN)<sub>4</sub><sup>2-</sup>, proves the presence of cobalt.

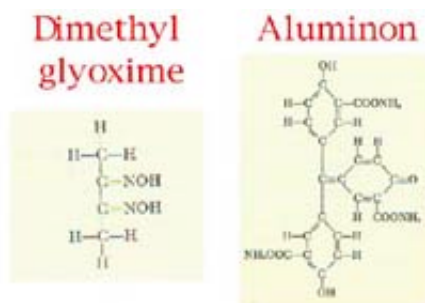
### Procedure 20: Separation and detection of Aluminum

Treat the decantate from Procedure 16 with 16 M HNO<sub>3</sub> [hood] until slightly acid, then add 15 M NH<sub>4</sub>OH [A-8] until distinctly alkaline; continue the stirring of the *ammoniacal* solution for 1 minute.

Centrifuge and decant, saving the decantate for Procedure 21. Because the Al(OH)<sub>3</sub> precipitate is gelatinous, highly translucent, very finely divided, and the color of opaque, bluish-white glass, its presence, suspended in the solution, is not easy to detect. On centrifuging however, it will appear in the bottom of the test tube as a whitish, jelly-like, opaque precipitate.

Wash the precipitate three times with hot water, then dissolve it in 5 drops of 3 M HNO<sub>3</sub> [A-6]. (If any precipitate fails to dissolve, remove it by centrifuging and decantation.)

Add 3 drops of Aluminon solution [B-3], mix thoroughly, make *just barely alkaline* with 5 M NH<sub>4</sub>OH [A-9], again mix thoroughly, then centrifuge. A **cherry red** precipitate (a so-called lake of Al(OH)<sub>3</sub> and adsorbed Aluminon) proves the presence of Aluminum.



### Procedure 21: Separation and detection of Chromium and Zinc

Follow (A) if the decantate from Procedure 20 is colorless; follow (B) if it is **yellow**.

(A) If the decantate is colorless, make the decantate just acid with 6M HCl [A-2]. Then add 4 drops of 0.2 M  $\text{K}_4\text{Fe}(\text{CN})_6$  [D-3] and mix thoroughly. The resulting mixture should be acidic. A grayish-white to bluish-green precipitate ( $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$ ) proves the presence of Zinc.

(B) If the decantate is **yellow**, add 7 drops of 0.2 M  $\text{BaCl}_2$  [C-2] to the **yellow** decantate, mix thoroughly, centrifuge until the supernatant liquid is clear (**clear does not mean colorless**), and decant, saving the decantate for Part (C) below. Wash the precipitate ( $\text{BaCrO}_4$ , mixed with some  $\text{BaSO}_4$ ) twice with hot water, add 3 drops of 3 M  $\text{HNO}_3$  [A-6], heat in the water bath and stir for about one minute.

Add 10 drops of cold water, mix thoroughly, cool under the cold water tap, add 1 drop of 3%  $\text{H}_2\text{O}_2$  [C-6]. Mix well by vigorous stirring and allow to settle. A **blue** coloration due to Chromium peroxide ( $\text{CrO}_5$ ) proves the presence of chromium.

(C) Make the decantate from (B) acid with 6 M HCl [A-2]. Then add 4 drops of 0.2 M  $\text{K}_4\text{Fe}(\text{CN})_6$  [D-3] and mix thoroughly. The resulting mixture should be acidic. A grayish-white to bluish-green precipitate,  $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$ , (pronounced *zinc potassium ferrocyanide*) proves the presence of Zinc.

*Here Endeth the Aluminum-Nickel Group*