

Experiment 2 Qualitative Analysis

Goals

To use Le Chatelier's principle, complex ion chemistry, and precipitation reactions in the determination of ions in solution. We will study two groups of ions. The first group is called Group I and includes NH_4^+ , Ag^+ , Cu^{2+} , and Bi^{3+} . The second group of ions is called Group II and includes Mn^{2+} , Ni^{2+} , Fe^{3+} , Al^{3+} , and Zn^{2+} .

Discussion

Qualitative analysis is a set of methods used in separating a mixture of ions and then identifying each ion in the mixture. Suppose we have a sample of water with two different ions like silver(I) and copper(II). In order to determine that each ion is dissolved in the water we separate the two ions and then perform an analysis of each separately. We can take advantage of the fact that silver ions (Ag^+) and copper ion (Cu^{2+}) have chemical reactivities that are not identical. We take advantage of chemical differences to separate and identify each ion. In this experiment we will separate and determine the name of ions in two mixtures, which we'll call Group I and Group II. Don't confuse these designations with the group numbers used in the periodic table. It is important that you keep a detailed record of your procedure so that any errors can be traced and corrected. In addition to detailed separation and identification instructions, flow charts and sets of equations are provided to help you understand the logic and the chemistry of the method. Before discussing the procedure of this experiment we will cover the topic of recording observations. You will receive a handout for recording observations. Keep the handout for all four meetings of the qualitative analysis component of this course. The handout looks like:

Chemistry 12

QUALITATIVE ANALYSIS RECORD OF OBSERVATIONS

Name _____ Section _____

Step #	Material Treated	Reagent	Color of Precipitate	Color of Solution	Equations and Conclusions (Note: Only one equation per line)	Sig.
A1	Group I known	3M NaOH	Gray/green	light green	$\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$	

Procedure for keeping a record of your results

Record each step you perform as well the result of each step. Whenever you add a material, heat a material, or cool a material record the step and what you observe happening.

The function of each column in the "Record of Observations" is shown below:

Step #: These are numbers in consecutive order starting with "A." Write a step when you add anything to your centrifuge test tube, including water or heat.

Material Treated: This is the material to which you add reagents. For example, the first material treated is "Group I known." Suppose during the analysis you produce a precipitate in the fourth step, and you then add a reagent to the precipitate. Now you are in step 5 and the material treated in step 5 is "P4." The solution from step 4 would be called "S4."

Reagent: This is the substance that you add to either a precipitate or a solution. It might be "6M HCl," "cold water," "heat," or "pH indicator paper." You don't need to list the amount you added.

Color of precipitate: You should also include the way it looks if you think it looks strange, such as "gelatinous." If an indicator paper is used, describe what color it turns in the "Equations and Conclusions" column.

Color of Solution: You should also state whether the solution is clear or cloudy.

Equations and/or Conclusions: In this space you must write all the balanced chemical equations for all the reactions taking place for this step. Also, if you can come to any conclusions about the identity of a substance, you should indicate it here. The equations are all listed in another section of this experiment. Since the equations may take up more than one line, you must leave space in the other columns. In other words, the equations must correspond to the appropriate step. Write only one equation per line.

Sig: This is the initial of your instructor for the known mixtures only. The signature is obtained when you show your instructor a confirmatory test for an ion (the shaded boxes in the flow diagrams) and have made all the entries in the appropriate columns. You must show your confirmatory test and filled out "Report of Observations" to your instructor as you do them. Don't save them all to the end or you will be asked to redo the known.

You must obtain signatures as indicated above. When you have obtained all the signatures for a known sample, and have filled in what you have done and seen in each step, and have written the balanced chemical equations, you may then receive an unknown sample.

You do not need to show your instructor anything while working on your unknown. You also do not need any signatures. However, after you have finished analyzing your unknown, you will need to show your instructor a completely filled out "Record of Observations," complete with balanced chemical equations. You will also have to give your instructor a completely filled out yellow report sheet. If your "Record of Observations" is correct, then your instructor will initial the yellow report sheet and keep it for grading.

Schedule for qualitative analysis

First meeting: Group I known solution. This solution has four ions. You will use the procedures described in the procedure section to identify the presence of each of the four ions.

Second meeting: Group I unknown solution. This solution has some combination of the ions tested in the first meeting. Your goal is to determine which ions are present in the solution using the procedure described in the procedure section.

Third meeting: Group II known solution. This solution has five ions that are different from the first two meetings. You will use the procedures described in the procedure section to identify the presence of each of the five ions.

Fourth meeting: Group II unknown solution. This solution has some combination of the ions tested in the third meeting. Your goal is to determine which ions are present in the solution using the procedure described in the procedure section.

Tips for performing qualitative analysis experiments

1. Balance the centrifuge. Also, check the centrifuge to be sure that stray centrifuge test tubes aren't in it.
2. Stir solutions in test tubes with a glass stirring rod. Don't put the stirring rod down on the lab bench. Store it in a beaker full of water.
3. Use short strips of pH paper to test for acidity. Test the acidity of a solution by dipping a glass stirring rod into the solution and then touching the tip of the rod to the indicator paper.

The color code for the test paper is:

red = very acidic (pH 1-2)
orange/yellow = moderately acidic (pH 3-6)
light green = neutral (pH 7-8)
dark green = moderately basic (pH 9-10)
blue = very basic (pH 11-12)

4. A common reagent we will use is ammonium hydroxide. There are a couple of ways to represent the chemical formula for this compound: NH_4OH and $\text{NH}_3 \cdot \text{H}_2\text{O}$.

Parts 1 and 2. The Separation and Confirmation of Group I Ions: NH_4^+ , Ag^+ , Cu^{2+} , Bi^{3+} . This procedure can be used for the known solution or the unknown solution.

Materials

Plastic centrifuge test tubes, glass stirring rod, centrifuge, pH indicator paper, group I known or unknown solution, sodium hydroxide solution, ammonium hydroxide solution, tin(II) chloride (SnCl_2) solution, hydrochloric acid solution, potassium hexacyanoferrate(II) ($\text{K}_4[\text{Fe}(\text{CN})_6]$) solution.

Procedure

1. Place 15 drops of the Group I solution in one centrifuge test tube and 5 drops in another centrifuge test tube. Be careful not to get any solution on the lip of a test tube because this will cause the pH indicator paper to give a false reading.
2. Confirmation of NH_4^+

To the centrifuge test tube with 5 drops of the Group I solution, add 10 drops of 3M NaOH being very careful not to get any of the solution on the mouth of the tube. Place a piece of wet pH indicator paper on the top of the tube. Heat the tube in boiling water.

If the universal indicator paper turns blue or blue-green, the presence of NH_4^+ is confirmed. Another method you might consider is to gently waft the fumes from the tube toward your nose. The odor of ammonia will confirm NH_4^+ .

The equation for the formation of ammonia gas is: $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$

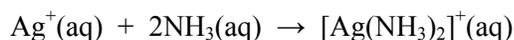
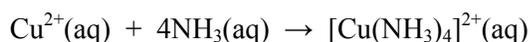
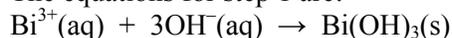
B. Separation and Confirmation of Bi^{3+}

1. Add 15 drops of 6M $\text{NH}_3 \cdot \text{H}_2\text{O}$ to the centrifuge test tube with 15 drops of Group I solution. Stir and centrifuge for two minutes. Add two more drops of 6M ammonium hydroxide to check that complete precipitation of the $\text{Bi}(\text{OH})_3$ has occurred. Stir, centrifuge, and decant (pour off) the supernatant (the liquid above the precipitate) into another tube. Label and save both tubes. You will use the supernatant in part C.

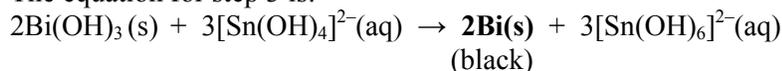
2. Add 20 drops of distilled water to the precipitate and stir. This is to wash the precipitate free of any contamination. Centrifuge the solution and decant the rinse water into the sink.

3. Add 10 drops of 0.1M SnCl_2 and 10 drops of 3M NaOH to the remaining precipitate. Stir and centrifuge the solution for two to three minutes. If you don't get a black precipitate, try adding another 10 drops of each reagent. Then stir and centrifuge the solution again. A black precipitate confirms the presence of Bi^{3+} .

The equations for step 1 are:



The equation for step 3 is:



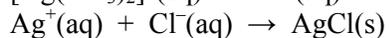
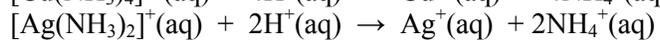
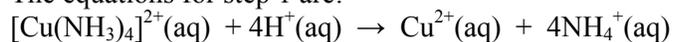
C. Separation and Confirmation of Ag^+

1. Add 10 drops of 6 M HCl to the supernatant in part B and stir the solution. Check to make sure that the solution is acidic using indicator paper. If it is not acidic, add two drops of 6M HCl and test again. Repeat until the solution is acidic. A white precipitate shows that Ag^+ is most likely present. Centrifuge, decant, and save the supernatant for part D. If copper ions are present, the solution may appear light blue due to the presence of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.

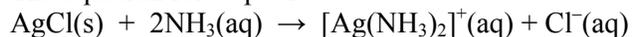
2. Add 20 drops of distilled water to the white precipitate. Stir and centrifuge the solution. Discard the water. Rinse a second time with 20 drops of water and centrifuge again. Decant the rinse water into a clean centrifuge test tube. Add 5 drops of 6M $\text{NH}_3 \cdot \text{H}_2\text{O}$ to the rinse water. If the rinse water turns blue, you must rinse the precipitate repeatedly until the rinse water doesn't turn blue upon the addition of ammonia. The rinsing is to remove copper(II) ions, which cause the blue color.

3. Add 20 drops of 6M $\text{NH}_3 \cdot \text{H}_2\text{O}$ To the remaining precipitate. Stir the solution. If the precipitate dissolves, then you have confirmed that Ag^+ is present.

The equations for step 1 are:



The equation for step 3 is:



D. Confirmation of Cu^{2+}

There are two tests to confirm the presence of copper(II) ions.

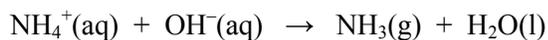
1. The first confirmation test: To one-half of the supernatant you saved from part C, add 10 drops of 6 M $\text{NH}_3 \cdot \text{H}_2\text{O}$. A dark blue solution confirms the presence of Cu^{2+} .

2. The second confirmation test: To the other half of the supernatant, add 4 drops of 0.1 M $\text{K}_4[\text{Fe}(\text{CN})_6]$. Centrifuge. A reddish-purple ppt confirms the presence of Cu^{2+} .

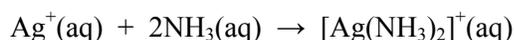
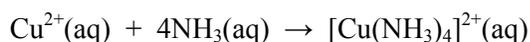
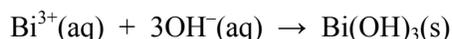
A note about copper: The $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion has a pale blue color and is the predominant form of copper in aqueous solutions. However, to simplify formula writing, we will usually write it as Cu^{2+} .

The Chemistry of the Group I Analysis

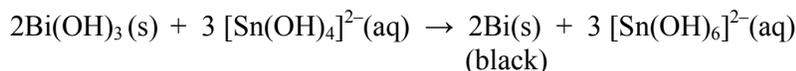
A. The ammonium ion is a weak base and is stable in an acidic solution. When it is made basic by the addition of sodium hydroxide, ammonia gas is formed. With gentle heat, the ammonia gas is driven off and can be detected by odor or by its turning universal indicator paper blue.



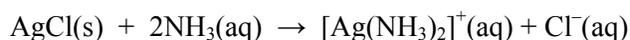
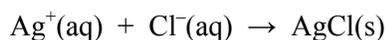
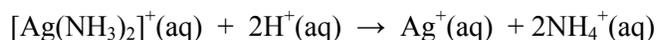
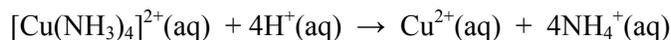
B. Aqueous ammonia precipitates Bi^{3+} as a white hydroxide. It also reacts with Cu^{2+} to form a deep blue tetraammine copper(II) complex ion, and with Ag^+ to form the diamminesilver(I) complex ion.



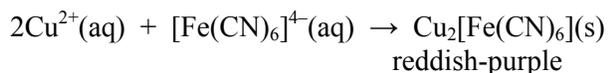
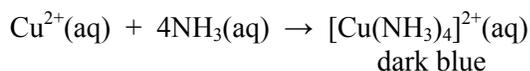
When a freshly prepared solution of sodium stannite is added to the bismuth hydroxide precipitate, the bismuth ion is reduced to metallic bismuth. The sodium stannite is made by mixing tin(II) chloride and sodium hydroxide directly in the ctt containing the bismuth hydroxide ppt.



C. The hydrochloric acid breaks up the complexes of copper and silver and precipitates white silver chloride. To be sure that the precipitate is really silver chloride, add ammonia (6M $\text{NH}_3 \cdot \text{H}_2\text{O}$). If the ppt is silver chloride, it will dissolve to form the diammine silver(I) complex ion.



D. The addition of ammonia to a Cu^{2+} solution causes the formation of the dark blue complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$. When potassium hexacyanoferrate(II) is added to a Cu^{2+} solution, a reddish precipitate of copper(II) hexacyanoferrate(II) is formed.

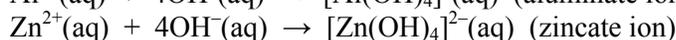
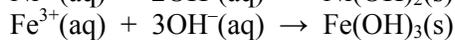
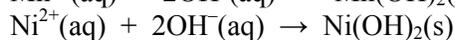
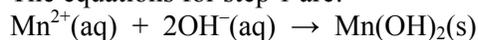


Parts 3 and 4: The Separation and Confirmation of Group II Ions: Mn^{2+} , Ni^{2+} , Fe^{3+} , Al^{3+} , and Zn^{2+} . This procedure can be used for the known or unknown solution.

A. Separation of Mn^{2+} , Ni^{2+} , and Fe^{3+} from Al^{3+} and Zn^{2+}

1. Place 20 drops of the Group II (known or unknown) solution into a clean centrifuge test tube and add 20 drops of 3M NaOH. Heat in a boiling water bath for 10 min. While heating, be sure to stir about every minute or so to mix the reagents or the aluminum and zinc won't precipitate properly. Stir, centrifuge, and decant the supernatant into a clean tube.
2. To reduce problems with the analysis for zinc and aluminum ions it is important that you not transfer any precipitate to the supernatant. If you have any question about the purity of the supernatant, centrifuge and decant it a second time. If you can't remove traces of precipitate by centrifuging, see your instructor who will use two disposable polyethylene pipets to filter the solution.
3. Save the precipitate and the supernatant. Label the supernatant "Aluminum and Zinc."

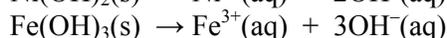
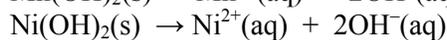
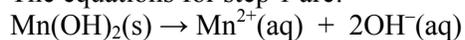
The equations for step 1 are:



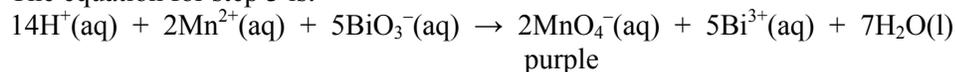
B. Separation and Confirmation of Mn^{2+}

1. To the tube containing the precipitate from part A, add 12 drops of 6M HNO_3 . Stir the solution until the precipitate dissolves.
2. Place 5 drops of this solution into another clean centrifuge test tube and add a small amount of solid sodium bismuthate (NaBiO_3) using a wooden spatula. Use the amount you can fit on the tip of the spatula.
3. Add 20 drops of distilled water, stir, and centrifuge. A purple-colored solution confirms the presence of Mn^{2+} .

The equations for step 1 are:



The equation for step 3 is:

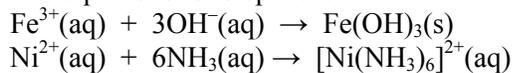


C. Separation and Confirmation of Fe^{3+}

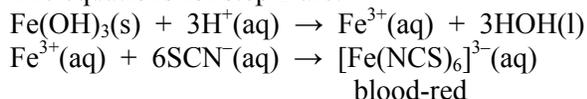
1. To the remaining solution from part B above, add 15 drops of 6M $\text{NH}_3 \cdot \text{H}_2\text{O}$ and stir. Centrifuge and decant the supernatant into a clean centrifuge test tube. Label the tube "Nickel" and set it aside for future use.

2. To the precipitate, add 10 drops of 6M hydrochloric acid, stir, and then add 3 drops of 0.1 M NH_4SCN . A "blood-red" color confirms the presence of Fe^{3+} .

The equations for step 1 are:



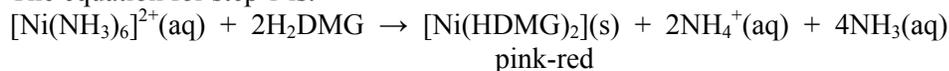
The equations for step 2 are:



D. The Confirmation of Ni^{2+}

1. Add 4 drops of dimethylglyoxime (DMG) to the tube labeled "Nickel" in part C and stir. There is no need to centrifuge, as the nature of the precipitate (sometimes called a "lake"), is more obvious before centrifuging. A strawberry-colored ppt confirms the presence of Ni^{2+} .

The equation for step 1 is:



E. Separation on Confirmation of Al^{3+}

1. Add 10 drops of 6 M HNO_3 to the solution from part A above labeled "Al & Zn" and stir. This will breakup the hydroxide complexes.

2. Now add 10 drops of 6M $\text{NH}_3 \cdot \text{H}_2\text{O}$ to the solution and stir. Check the solution with universal indicator paper to be sure it is basic (dark blue).

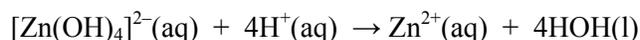
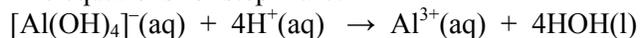
3. If the solution is acidic, add 10 more drops of 6M $\text{NH}_3 \cdot \text{H}_2\text{O}$. Stir and re-check the acidity of the solution. Continue adding 6M $\text{NH}_3 \cdot \text{H}_2\text{O}$ until the solution is basic. You should get a clear gelatinous precipitate. It may be hard to see until the tube is centrifuged. Even then, some people have difficulty seeing the precipitate.

4. Centrifuge and decant the supernatant into a clean tube. Label this tube "Zinc."

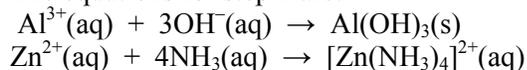
5. Add 5 drops of 6M HNO_3 to the precipitate that supposedly contains aluminum(III) ions and stir until it dissolves. If it looks like a precipitate is still present, test the solution for acidity with pH paper. If the solution is not acidic, add 6M HNO_3 one drop at a time, with stirring, until the solution is acidic.

6. Now add 4 drops of aluminon reagent and 10 drops of 6 M $\text{NH}_3 \cdot \text{H}_2\text{O}$. Stir and centrifuge. A cherry-colored precipitate confirms the presence of Al^{3+} .

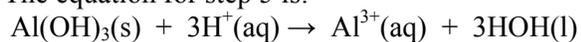
The equations for step 1 are:



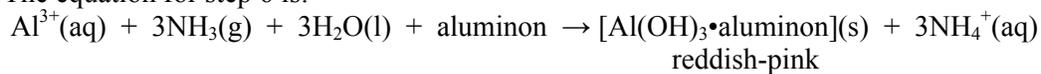
The equations for step 2 are:



The equation for step 5 is:



The equation for step 6 is:

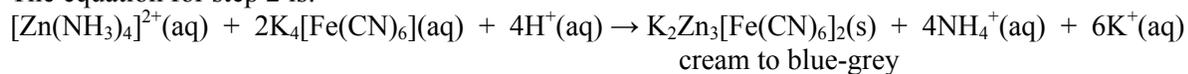


F. Confirmation of Zn^{2+}

1. Add 10 drops of 6 M hydrochloric acid to the supernatant from part E above labeled "Zinc." Stir the solution.

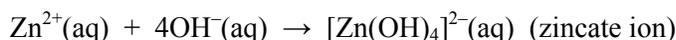
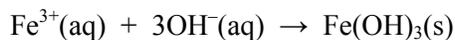
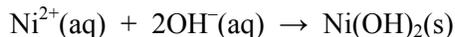
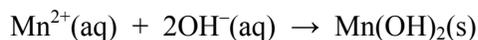
2. Add 4 drops of 0.1M $\text{K}_4[\text{Fe}(\text{CN})_6]$. Stir and centrifuge the solution. A cream-colored precipitate confirms the presence of Zn^{2+} . Note: This precipitate may be contaminated with iron from part A and may be various shades of blue depending on how much contamination is present.

The equation for step 2 is:

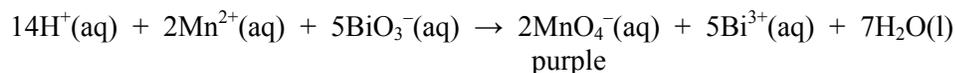
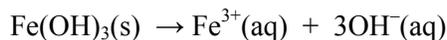
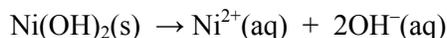
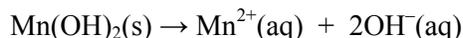


The Chemistry of the Group II Analysis

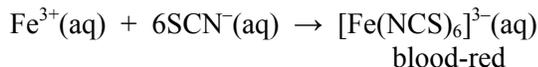
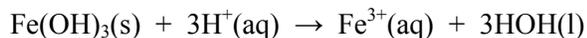
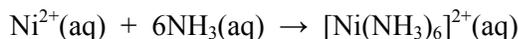
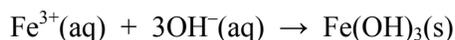
A. The addition of sodium hydroxide does two things: (a) It precipitates the hydroxides of manganese, nickel, and iron. (b) It forms the hydroxide complexes of aluminum and zinc, since these hydroxides are amphoteric.



B. The addition of nitric acid dissolves the hydroxide precipitate. When sodium bismuthate, a strong oxidizing agent, is then added, the Mn^{2+} ion is oxidized to the permanganate ion.



C. The addition of ammonia forms a precipitate of iron(III) hydroxide and the hexaamminenickel(II) complex ion. Upon the addition of hydrochloric acid to the precipitate, it dissolves giving Fe^{3+} ions in solution. Then treating this solution with ammonium thiocyanate forms a blood-red precipitate of the hexaisothiocyanatoferrate(III) complex ion.

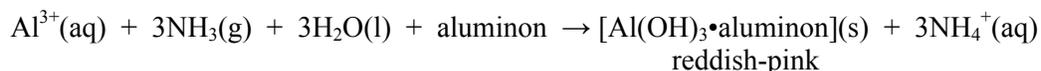
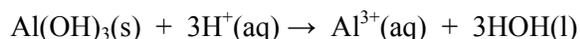
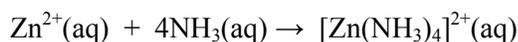
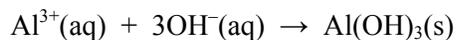
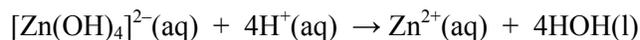
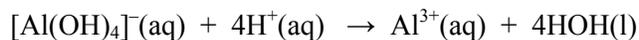


D. Adding dimethylglyoxime, H_2DMG , to the solution of hexaamminenickel(II) ion gives another complex ion commonly called nickel dimethylglyoxime. [Note: Dimethylglyoxime (H_2DMG , 2,3-butanedionedioxime, $\text{C}_4\text{H}_8\text{N}_2\text{O}_2$) is an organic complexing agent that causes a colorful precipitation of nickel ions.]

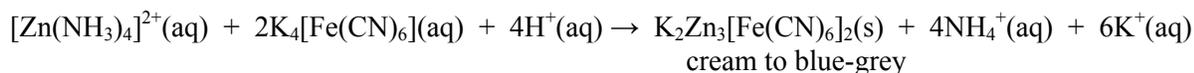


E. The addition of nitric acid will break up the hydroxide complexes of aluminum and zinc. Then the addition of ammonia to the resulting solution of Al^{3+} and Zn^{2+} ions will do two things: (a) the aluminum

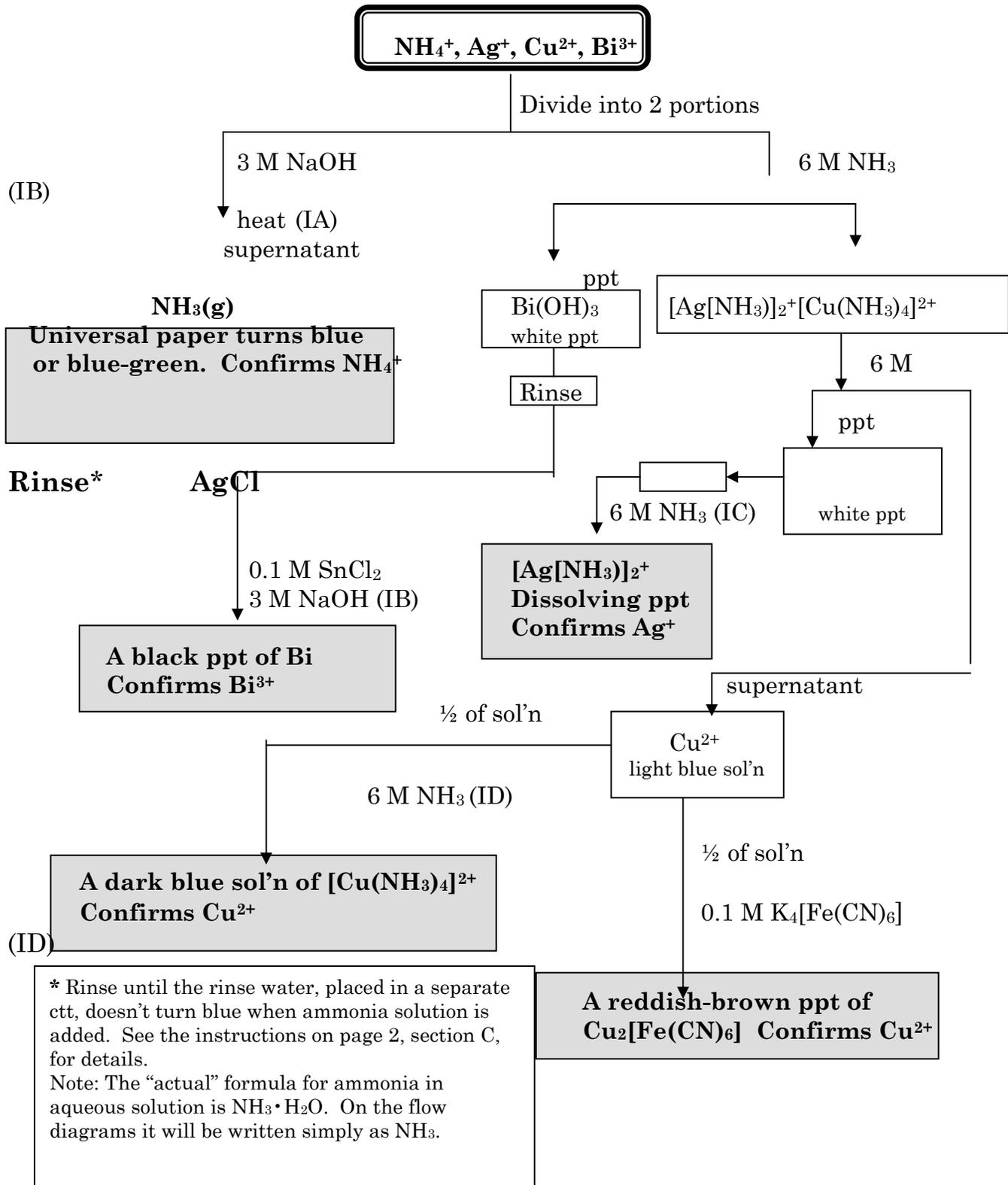
ion will precipitate as aluminum hydroxide and (b) the zinc ion will form the tetraamminezinc(II) complex ion. Now nitric acid is added to the aluminum hydroxide precipitate causing it to dissolve. Then the addition of ammonia and aluminon reagent will cause a reddish-pink precipitate of $[\text{Al}(\text{OH})_3 \cdot \text{aluminon}]$ complex to form. (Note: The aluminon reagent is the ammonium salt of aurin tricarboxylic acid, $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_9$, a red dye.)



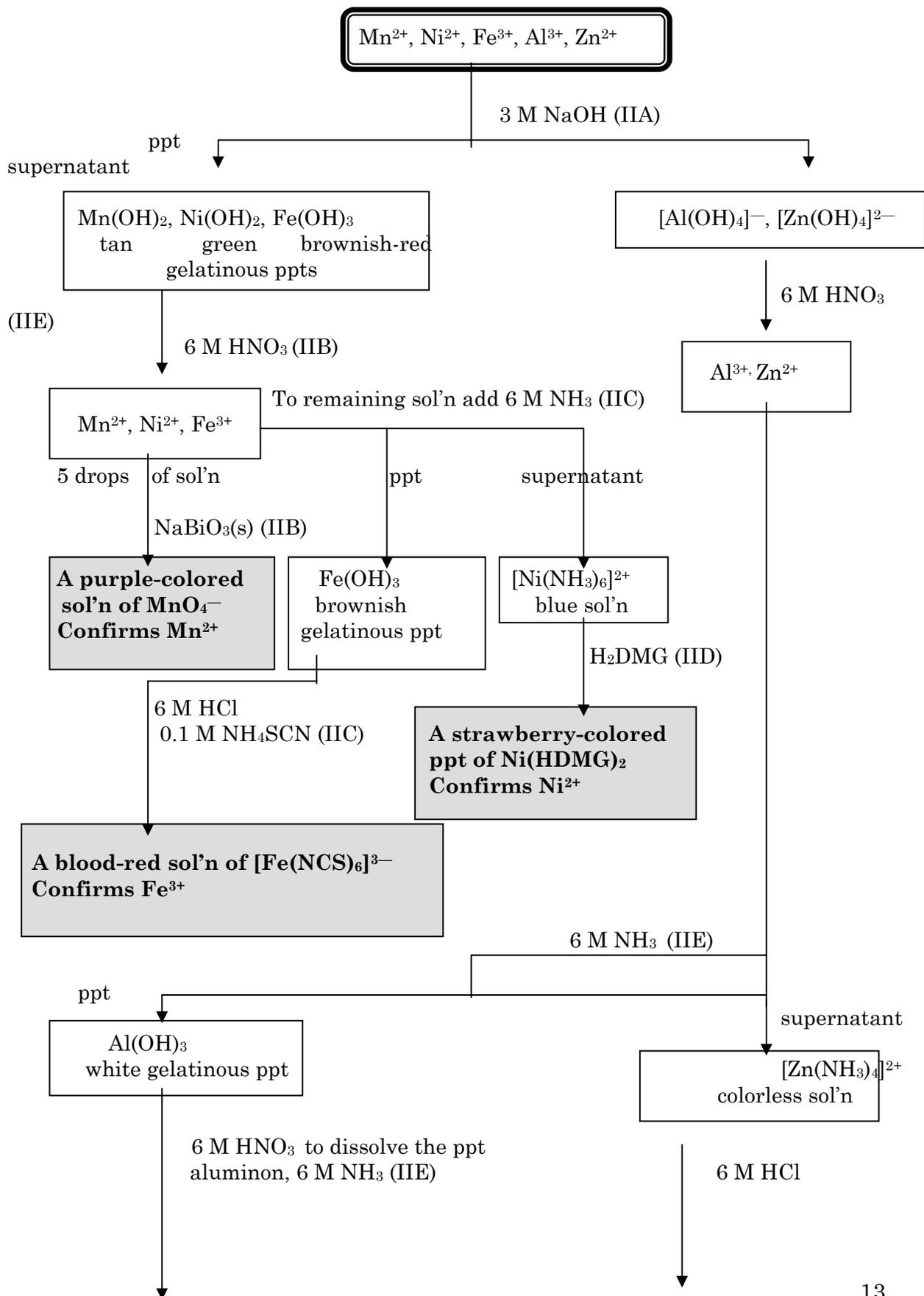
F. The addition of HCl breaks up the tetraamminezinc(II) complex ion. Then the addition of potassium hexacyanoferrate(II) forms a precipitate of $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]$. These two reactions are shown as one step below.



Group I Flow Chart



Group II Flow Chart





$K_4[Fe(CN)_6]$ (IIF)
A cherry-colored ppt
of $[Al(OH)_3 \cdot \text{aluminon}]$
 $K_2Zn_3[Fe(CN)_6]_2$
Confirms Al^{3+}
blue-
iron.
iron.



A cream-colored ppt of
Confirms Zn^{2+} Note: This ppt may be
colored due to contamination with
colored due to contamination with