

Qualitative Inorganic Analysis

Objective

To identify ions that are present in unknown solutions and solids using "wet chemical" separation methods. These methods are based on the behavior of different ions when they react with certain reagents. Reagents are substances chosen because of their chemical activity with the ions being analyzed. Learning the chemistry that governs the identifications is an important part of this experiment.

Principles

All measurements are all comparisons against references. We normally talk about quantitative measurements of meters, kilograms, and second. But qualitative measurements are no different. In this experiment, you compare the chemical changes you observe in a known sample with observations on your unknown sample to determine the identity of the anions and cations in the unknown. You'll start with a sample known to contain all 9 cations and an unknown with 4-6 cations.

In the classical analytical scheme the chemical properties of the different ions, both positive ions (cations) and negative ions (anions), are used to separate a mixture of them into successively smaller groups of ions, until some characteristic reaction may be used to confirm the presence or absence of each specific ion. In addition to analyzing the unknown for its component ions, the qualitative analysis scheme highlights some of the important chemical behavior of these metal salts in aqueous solution. The concepts of chemical equilibrium are emphasized, as illustrated by precipitation reactions, acid-base reactions, complex-ion formation, and oxidation-reduction reactions. Each experiment presents a puzzle that is solved "detective fashion" by assembling a collection of chemical clues into an airtight case for the correct identifications. As a bonus, the clues often take the form of colorful solutions and precipitates.

The qualitative analytical scheme is divided into three parts:

1. Separation and identification of cations.
2. Identification of anions.
3. Identification of an unknown in which both a cation and anion are present.

Overview of cation separation process:

1. Separate cations that form insoluble chlorides (Ag^+ , Pb^{2+})
2. Separate cations that have highly insoluble hydroxides that precipitate when the hydroxide ion concentration is small, approximately $10^{-5} M$. (Fe^{3+} , Cr^{3+} , Al^{3+})
3. The remaining 4 cations (Ba^{2+} , Mg^{2+} , Cu^{2+} , Ni^{2+}) cations all precipitate at when the hydroxide ion concentration increases to $0.01 M$ so we add SO_4^{2-} to remove the Ba^{2+} as BaSO_4 . Next add ammonia to form complex ions ($\text{Cu}(\text{NH}_3)_2^{2+}$ and $\text{Ni}(\text{NH}_3)_2^{2+}$. These complex ions are more stable than are the hydroxides so we can add hydroxide ion to precipitate Mg^{2+}
4. We have a mixture of Cu^{2+} , which we detect by adding iodide and Ni^{2+} , which is detected by adding a reagent called dimethylglyoxime.

Schedule

Experiment	Due After Lab Meeting
Cation Known and Unknown from Flowsheets 1-2	1
Cation Known and Unknown from Flowsheets 3-4	2
General Unknown from Flowsheets 1-4	2
Anion Known and 2 Unknowns and Salt mixture	3

Recording Observations.

All observations and conclusions should be recorded in your lab notebook. Record information for both your known samples and unknown samples using the results for the known samples as a guide to identify the unknowns. In Part 2, Anion Analysis, either recreate Table 2 from page 17 of this experiment in your notebook, or print an extra copy and tape it into your lab notebook. An accurate, thoughtful record is important. Understanding the chemistry and a little forethought will minimize errors.

Laboratory Reports.

When you and your partner have identified the ions present in each of your unknown samples to your satisfaction, report it on a sheet of paper to your Laboratory Assistant to be graded. Include your name, your lab partner's name, the unknown number, and the identity of ions.

General Techniques.

The usual reactor vessel on this scale is the 10 x 75 mm test tube. The quantities of solution handled are of the order of one to two milliliters, and the volumes of reagents to be added are on the order of one to several drops (~ 0.05 mL). Convenient reagent containers to use in this laboratory experiment are located on the side shelf.

- 1. Separation of precipitates from solutions**—the principal separation method used is precipitation. This separation is performed using a centrifuge, which spins the sample in a small test tube at high speeds, causing the precipitate to settle rapidly to the bottom of the tube. When using the centrifuge always counterbalance the sample tube with a test tube containing water filled to the same level as the sample. Always place the cover on the centrifuge before turning it on (if a tube breaks, those nearby won't be hit by flying glass). Allow the centrifuge to coast to a stop. Do not attempt to slow it with your fingers. With most precipitates 30 - 60 seconds of centrifuging will be sufficient to obtain a good separation. If the solution still appears cloudy after this length of time, centrifuge for another minute or two. After centrifuging, most of the liquid may be poured into another container without disturbing the solid. This process is called decantation.
- 2. Washing a precipitate**—since decantation does not completely remove the solution it is recommended that the precipitate be purified further by washing. Add about 1 mL of water (or other recommended washing solution) into the tube containing the precipitate. Stir with a vertical motion with a stirring rod to suspend the solid in the washing solution. Centrifuge and decant the liquid.
- 3. Re-precipitation**—In some cases, particularly when the precipitate (ppt.) is gelatinous in nature, it may have to be dissolved and re-precipitated to remove salts that have been carried down with the gelatinous precipitate. The resulting solution, after centrifuging (centr.) and decantation, is added to the solution resulting from the first precipitation, or discarded.

4. **Adding reagents**—the reagents are measured in drops delivered from a dropper bottle. When adding reagents the tip of the dropper must never touch the test solution or the walls of the test tube. A contaminated reagent solution can cause erroneous results.

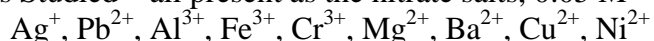
5. **Heating and Cooling Solutions**—at several places in the procedure it is necessary to heat samples. Never heat the test tube directly with a burner flame. Directly heating the test tube will invariably result in the entire sample "bumping" out of the test tube. The proper way to heat a sample is to place the test tube into a small beaker of water and gently heating the beaker. Cooling a sample is done in the same manner, using cold water or ice in a beaker.

6. **Testing for Completeness of Precipitation**—after adding the specified amount of a precipitating reagent it is suggested that a test for completeness of precipitation be carried out as follows. Centrifuge and without decanting the solution add a drop of reagent so it runs down the wall of the test tube. If precipitation is complete no new precipitate will form when the reagent dissolves in the solution.

7. **Discarding waste.** None of the solutions generated in this experiment goes down the sink. Discard all waste into the waste container and rinse the test tube once with water and discard the rinse into the waste container. Replace the cap on the waste container as soon as you finish, even if there is another person waiting to use it. Federal laws govern hazardous waste disposal.

Part 1. Cation Analysis

Cations Studied—all present as the nitrate salts, 0.05 M



Reagents

For Separations

HCl (dil., 6 M)
 HNO₃ (dil., 6 M)
 H₂SO₄ (dil., 6 M)
 NH₃ (dil., 7.5 M)
 NaOH (dil., 6 M)
 H₂O₂ (3 %)
 KI (2 M)
 Na₂SO₃ (saturated)

For Confirmatory Tests

KSCN (0.2 M)
 Aluminon reagent (Note 1)
 Na₂HPO₄ (0.2 M)
 Dimethylglyoxime (Note 2)
 NH₄NO₃ (5 M)
 K₂CrO₄ (0.2 M)
 BaCl₂ (0.2 M)

Note 1. Aluminon reagent (0.1 %) is prepared by dissolving 1 gram of ammonium aurintricarboxylate in a liter of distilled water.

Note 2. Dimethylglyoxime reagent (1%) is prepared by dissolving 10 grams of dimethylglyoxime in 1 liter of 95% ethyl alcohol.

Fresh hydrogen peroxide (H₂O₂)-and sodium sulfite (Na₂SO₃) should be obtained at the beginning of a laboratory period since on storage the peroxide tends to decompose and the sulfite may be oxidized to sulfate by dissolved oxygen.

General reference:

D. L. Reger, S. R. Goode and D. W. Ball, "Chemistry Principles and Practice", Third Edition, Cengage Publishing (Belmont CA) 2010.

Basis of the Qualitative Analytical Separations in this Scheme

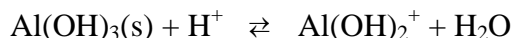
The separations used in this qualitative analytical scheme are based on the facts contained in an abbreviated set of solubility rules and the facts that some insoluble metal hydroxides dissolve in the presence of excess hydroxide ion (are amphoteric) and that some transition metal ions tend to form ammine complexes with ammonia.

Brief Solubility Rules

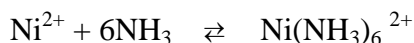
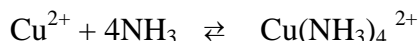
1. All nitrates are soluble.
2. All chlorides are soluble except AgCl , Hg_2Cl_2 and PbCl_2 .
3. All sulfates are soluble except SrSO_4 , BaSO_4 , Hg_2SO_4 , and PbSO_4 .
4. All carbonates are insoluble except those of the group 1 elements and NH_4^+ .
5. All hydroxides are insoluble except those of the group 1 elements and NH_4^+ , $\text{Sr}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$. $\text{Ca}(\text{OH})_2$ is slightly insoluble.

*Insoluble compounds here are defined as those which precipitate upon mixing equal volumes of solutions 0.1 M in the corresponding ions.

The nine cations included for analysis in this scheme are Ag^+ , Pb^{2+} , Al^{3+} , Fe^{3+} , Cr^{3+} , Mg^{2+} , Ba^{2+} , Cu^{2+} and Ni^{2+} , listed roughly in the order in which they are separated. Aluminum hydroxide is amphoteric; $\text{Al}(\text{OH})_3$ reacts with bases as well as acids. The reactions are:



The two cations in the group that tend to form complexes with ammonia under the conditions encountered in the laboratory are Cu^{2+} and Ni^{2+} . The reactions are:



Using these equilibria and the solubility rules, the seven cations will be separated into four groups

Group 1. Insoluble chloride salts (Ag^+ , Pb^{2+}). HCl is added to the soluble nitrate salts of the metal ions (rule 1) to precipitate AgCl and PbCl_2 .

Group 2 Highly insoluble hydroxide salts (Trivalent cations Al^{3+} , Cr^{3+} , and Fe^{3+}) Adding NH_3 makes the solution basic and precipitates the hydroxides of Al^{3+} , Cr^{3+} , and Fe^{3+} (rule 5). The excess NH_3 forms the soluble ammine complexes of Cu^{2+} and Ni^{2+} keeping them in solution. A portion of the added NH_3 reacts with the HCl from the first separation to form NH_4^+ (ammonium cation), forming a buffer solution with the unreacted NH_3 . This buffer prevents the hydroxide ion concentration from becoming large enough to precipitate the insoluble hydroxide $\text{Mg}(\text{OH})_2$.

Group 3 Divalent cations that do not form ammonia complexes (Ba^{2+} , Mg^{2+}). This group precipitates in two steps. BaSO_4 is precipitated by adding sulfuric acid (rule 3 of the solubility table). The ammonia concentration in the solution containing the remaining cations, Mg^{2+} , Cu^{2+} and Ni^{2+} is

increased to convert the last two cations into their ammine complexes, and NaOH is added to furnish a large enough hydroxide ion concentration that $\text{Mg}(\text{OH})_2$ now precipitates

Group 4 Divalent cations that form ammonia complexes (Cu^{2+} , Ni^{2+}) The precipitation of $\text{Mg}(\text{OH})_2$ leaves only the Group 4 cations in solution as $\text{Cu}(\text{NH}_3)_4^{2+}$ and $\text{Ni}(\text{NH}_3)_6^{2+}$.

The foregoing separations of the cations into groups, the separations within the groups and the specific tests for identification of the individual ions are described in more detail on the page after each Group flow diagram. Refer to these more detailed descriptions of the chemistry each step along the flow charts.

Characteristic Colors--Some of the transition metal compounds and complexes encountered here exhibit color. Attention to the colors (or their absence) of solutions and precipitates can often be quite helpful in deciding whether or not a particular ion might be present. The student should become familiar with the colors of the solutions and precipitates of the ions involved in the scheme. To this end, the colors of the ions, complexes, and precipitates encountered in this scheme are furnished below. Those ions that are colorless and those precipitates that are white are omitted from the following table.

<u>Ion or Precipitate</u>	<u>Color</u> _____
Fe^{3+}	yellow to orange
$\text{Fe}(\text{OH})_3$ (s)	red-brown
FeSCN^{2+}	red
Cu^{2+}	blue
$\text{Cu}(\text{NH}_3)_4^{2+}$	deep blue
Ni^{2+}	green – blue/green
$\text{Ni}(\text{NH}_3)_6$	violet

Flow Charts--The qualitative analytical scheme that follows is presented in the form of a flow chart. The student starts with a mixture of cations, as the soluble nitrates, page 12, all appearing in a rectangular box. Along a vertical line, just below the box, is the reagent to be added to the solution and its amount (2 d HCl). The 2 d HCl means that the student is to add two drops of dilute hydrochloric acid to the mixture in the box, with stirring. The vertical line in the diagram continues down to intersect with a horizontal line. This intersection means: centrifuge the solution after the above treatment, decant the supernatant solution into another test tube (indicated as a box to the right on the diagram, in this case solution 2A). The solid (Group) that is possibly precipitated by the reagent is indicated by an oval to the left on the diagram.

Both the known and unknown solutions will be analyzed by pairs of student. The experiment is initiated by analysis of a known solution containing all of the cations. The analysis of the unknown solutions using the following scheme sometimes leads to observations of very small quantities of precipitates and/or faint positive color tests for cations. Quite often these "trace" amounts are small amounts of impurities or precipitates resulting from interfering cations (or dirty glassware). In deciding whether the test for your unknown is positive or not, the student should compare the quantity of precipitate (or intensity of color) obtained with the unknown with that obtained in the analysis of a known solution; these should be comparable.

Remember that you need to **record your observations in your lab notebook**. You will be referring to it throughout the qual scheme because you have several different cation unknowns but you only run the known solution once.

Procedure

Safety Precautions. Wear approved eye protection and gloves. Work in pairs.

Week 1

1. Obtain a known test solution containing all of the cations. All of the cations are in the form of soluble nitrate compounds.
2. Obtain an unknown sample.
3. Follow the procedures on the flow charts for separating and identifying the cations. Note your observations on in your lab notebook. Be sure to refer to the page following each flow chart in order to understand the chemistry involved in the tests. Report the identities of the cations in Group 1 and 2 to your TA. Save the remaining solution from the known. It has the rest of the cations in it and will be used next week.

Week 2

1. Continue with your known and unknown samples, now containing metals in Groups 3 and 4, and use the procedures outlined on the flow charts to determine which ions are present. Record the ions and submit your result to your Teaching Assistant.
2. Obtain a general unknown sample that could contain metals in any of the Groups, and use the procedures outlined on the flow charts to determine the ions present. Record the ions and submit your result to your Teaching Assistant.

Notes that will help interpret the flow diagrams:

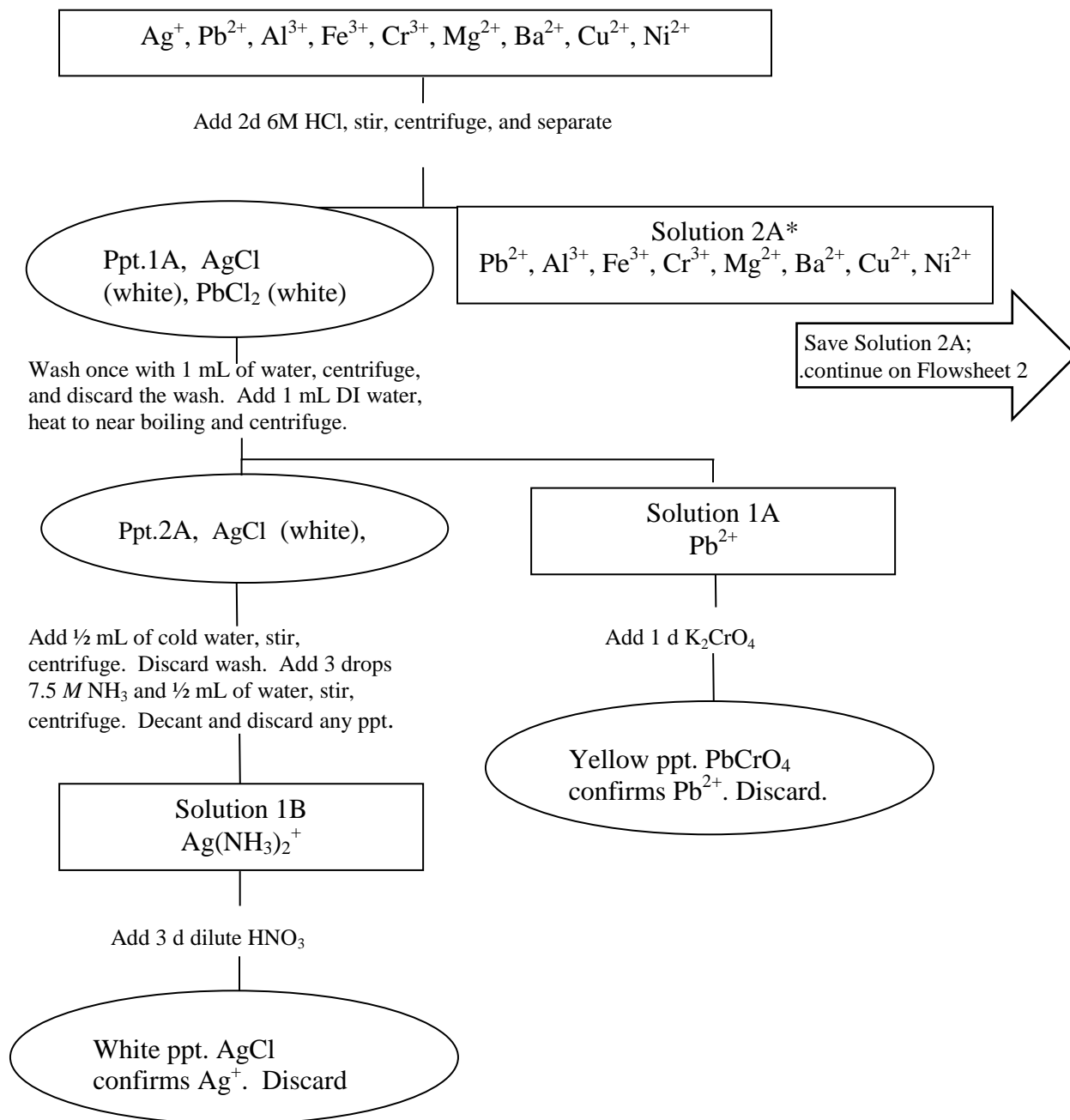
Any time the diagram splits, you should stir, centrifuge and separate.

Ovals are precipitates (ppt, solids) and rectangles are solutions.

Any time you are adding water to a test tube, it should be deionized water. Baths can be tap water.

Group 1- Precipitation and Identification of Silver and Lead.

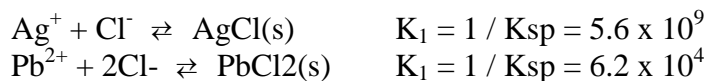
Start with 1 mL of the known and 1 mL of the unknown solution. Start all unknowns at the beginning.



*Solution 2A may have traces of Pb^{2+} as the K_{sp} for PbCl_2 is relatively high

**Chemical Equilibria and Reactions Involved in the Cation Scheme.
Group 1 - Separation and Identification of Silver (Ag⁺) and Lead (Pb²⁺).**

The reactions that occur when HCl is added to the solution are:



The large values of K (small values of K_{sp}) show that these compounds are classified as insoluble. The remaining cations do not have insoluble chlorides.

The confirmatory test for silver

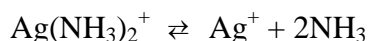
The white AgCl precipitate dissolves when ammonia is added to form the complex cation, diammine silver(I)



Adding nitric acid to the diammine silver reacts to remove ammonia, forming NH_4^+ , and the clear silver diammine complex is replaced by the white AgCl(s).

The pertinent chemical reactions are:

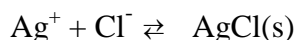
The silver diammine complex ion is in equilibrium:



Adding H^+ removes the NH_3



Leaving the silver ion to re-react with the residual chloride ion

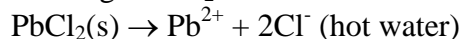


The net reaction is:

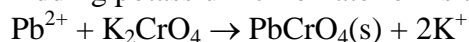


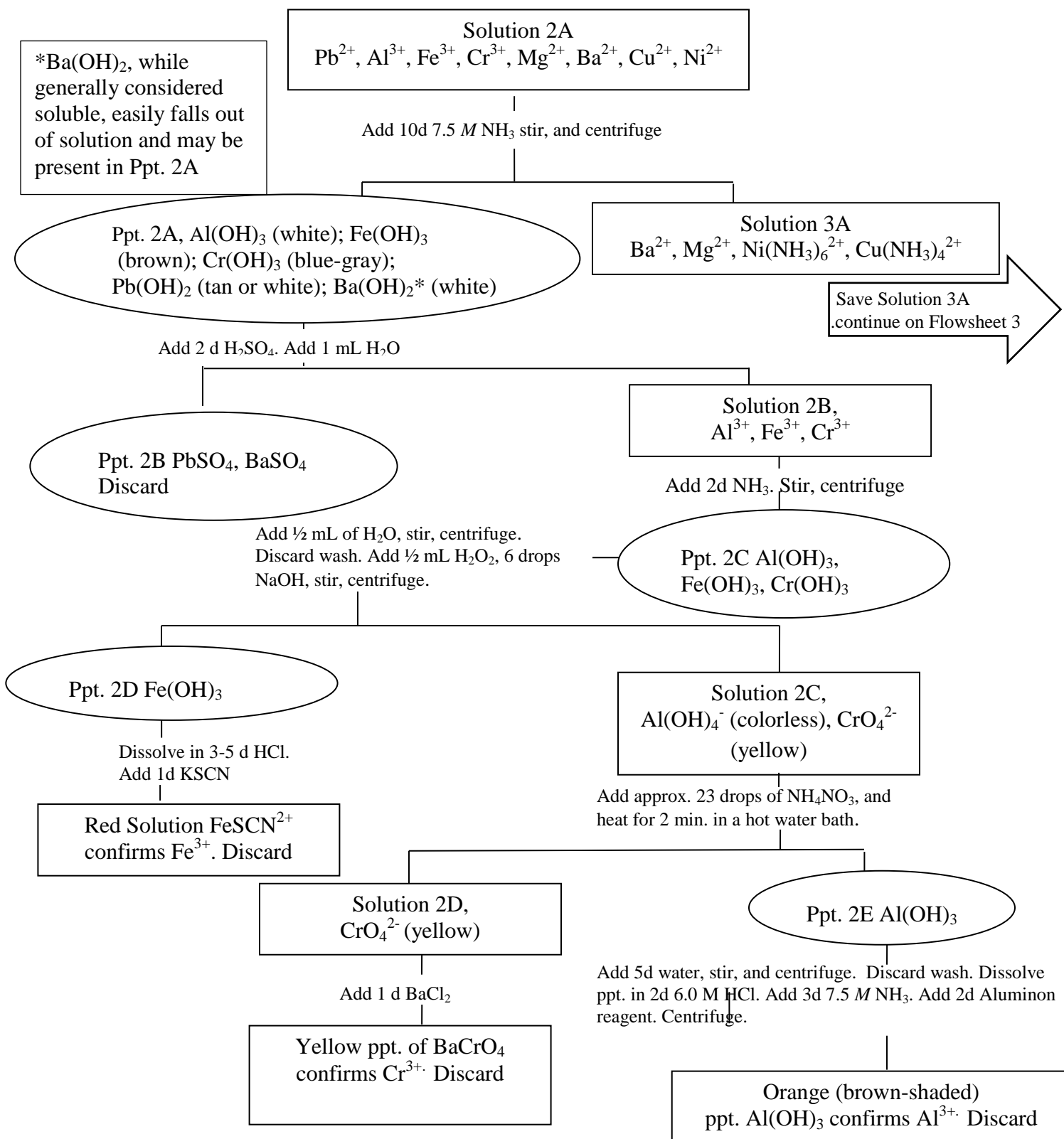
Confirmatory test for lead

Although PbCl_2 is insoluble in room temperature water, it dissolves in hot water.



Adding potassium chromate forms the bright yellow lead chromate:



Group 2 - Separation of Identification of Aluminum, Iron and Chromium.

Chemical Equilibria and Reactions Involved in the Cation Scheme. Group 2 - Separation and Identification of Al^{3+} , Fe^{3+} , and Cr^{3+}

This separation involves several factors:

- Formation of a buffer solution of NH_3 plus NH_4Cl to control the $[OH^-]$.
- Complex ion formation of Ni^{2+} and Cu^{2+} with ammonia.
- Precipitation of the hydroxides of Al^{3+} , Fe^{3+} , and Cr^{3+} that are insoluble under the conditions specified.

Some of the ammonia added at this point reacts with hydrogen ion, introduced as HCl in the precipitation of the silver, to form NH_4^+ . The excess NH_3 and the NH_4^+ so formed governs the hydroxide ion concentration through the equilibrium reactions



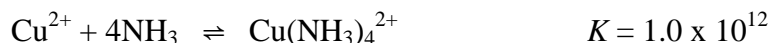
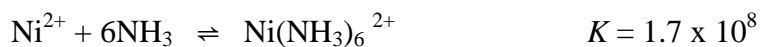
The solubility product constants for the hydroxides of the metal cations present at this point in the scheme are given in Table 1.

Table 1 . Solubility Products for Some Metal Hydroxides.

Reactions	K_{sp}
$Fe(OH)_3(s) \rightleftharpoons Fe^{3+} + 3OH^-$	2.6×10^{-39}
$Al(OH)_3(s) \rightleftharpoons Al^{3+} + 3OH^-$	5×10^{-33}
$Cr(OH)_3(s) \rightleftharpoons Cr^{3+} + 3OH^-$	6.7×10^{-31}
$Cu(OH)_2(s) \rightleftharpoons Cu^{2+} + 2OH^-$	1.6×10^{-19}
$Ni(OH)_2(s) \rightleftharpoons Ni^{2+} + 2OH^-$	5.5×10^{-16}
$Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^-$	8.9×10^{-12}

The $[OH^-]$ ($\sim 10^{-5}$ M in the final solution) is sufficient to result in the precipitation of the hydroxides of Al^{3+} , Fe^{3+} and Cr^{3+} as the hydroxides but the hydroxide concentration is not quite high enough to precipitate $Mg(OH)_2$. $Ba(OH)_2$ is relatively soluble.

The remaining cations, Ni^{2+} , and Cu^{2+} , are transition metals that form stable complex ions in the presence of excess NH_3 .



Fe^{3+} , Al^{3+} and Cr^{3+} do not form an ammine complex that is sufficiently stable to prevent precipitation of the hydroxide. Although Cu^{2+} and Ni^{2+} form insoluble hydroxides, they do not precipitate from this solution because nearly all of the Cu^{2+} and Ni^{2+} are tied up as the complex and the actual concentration of the free metal species is extremely low – too low to precipitate.

The copper-ammonia complex results in a deep blue solution and the nickel-ammonia complex is violet in solution.

Adding excess sodium hydroxide to the precipitate containing $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ dissolves $\text{Al}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ but not $\text{Fe}(\text{OH})_3$ or. Al^{3+} is amphoteric, that is, it tends to form a stable anionic complex with hydroxide ion.



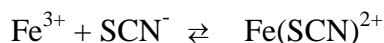
Along with the excess hydroxide, hydrogen peroxide is added, which dissolves the chromium hydroxide



The $\text{Fe}(\text{OH})_3$ ppt. dissolves readily in hydrochloric acid.

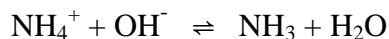
The confirmatory test for Fe^{3+}

Adding potassium thiocyanate to the Fe^{3+} solution results in formation of the deep red thiocyanatoiron (III) complex ion.



The confirmatory test for Al^{3+}

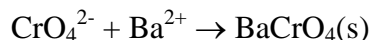
Adding NH_4NO_3 to the basic solution containing $\text{Al}(\text{OH})_4^-$ results in a significant reduction in the $[\text{OH}^-]$ due to the reaction



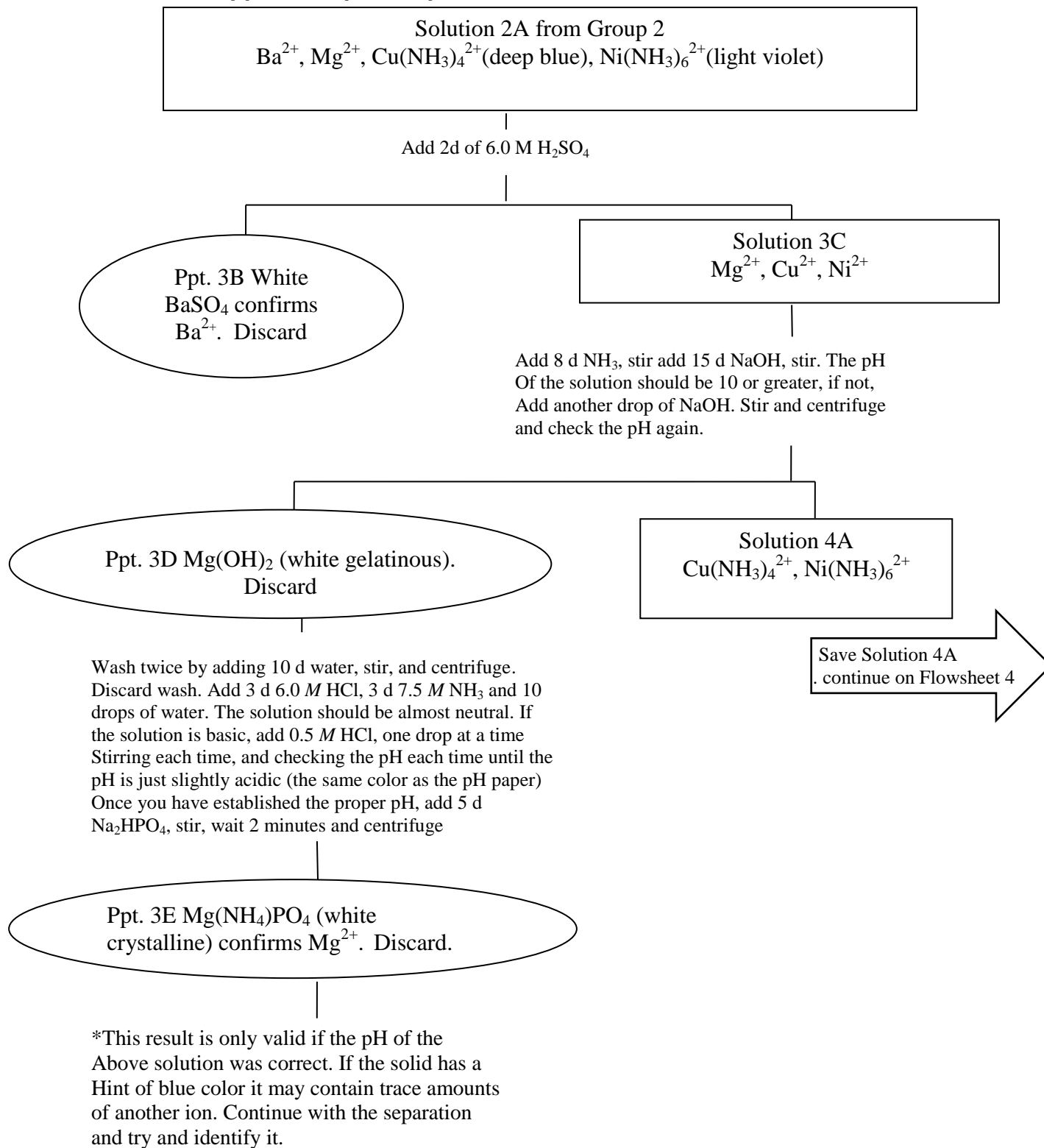
This reaction breaks up the $\text{Al}(\text{OH})_4^-$ complex and $\text{Al}(\text{OH})_3$ precipitates but the CrO_4^{2-} remains in solution. The $\text{Al}(\text{OH})_3$ precipitate is then re-dissolved in HCl and Aluminon, the ammonium salt of aurin tricarboxylic acid and ammonia are added to form an insoluble orange-tinged solid at pH 4 to 8. The ammonia precipitates $\text{Al}(\text{OH})_3$ and aluminon adsorbs to the gelatinous precipitate. The presence of this colored solid, called a "lake," confirms aluminum in the sample.

The confirmatory test for Cr^{3+}

The chromium is present, dissolved in solution, as CrO_4^{2-} . Adding barium chloride forms a yellow precipitate and confirms the presence of Cr^{3+} in the original sample.



3. Separation of the Group 3 Alkaline Earth Metal Cations From the Copper Group, Group 4



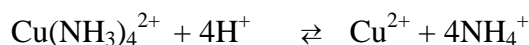
**Chemical Equilibria and Reactions Involved in the Cation Scheme.
Group 3. Separation of Barium and Magnesium.**

The addition of sulfuric acid to the solution remaining from the separation of the aluminum group results in precipitation of any barium present as white barium sulfate.

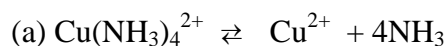


Confirmatory test for Ba²⁺

A white precipitate at this point confirms the presence of Ba²⁺. The acid also decomposes the transition metal ion-ammonia complexes that are present.



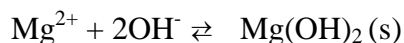
This reaction can be viewed as occurring in two steps: (a) the dissociation of the copper ammine complex,



and (b) the protonation of the free ammonia, greatly lowering the concentration of NH₃.



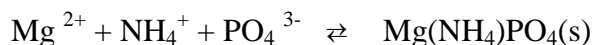
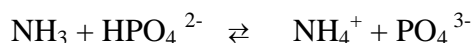
The solution (containing Mg²⁺, Cu²⁺ and Ni²⁺) is now treated with more NH₃, reforming the ammine-complexes of copper and nickel. The solution, containing ammonium sulfate and ammonia, has a [OH⁻] ~ 10⁻⁵ M, so magnesium hydroxide does not precipitate, until the solution is made decidedly basic with the addition of sodium hydroxide:



The gelatinous white Mg(OH)₂ will be contaminated with some occluded copper, and nickel. This occlusion will cause the precipitate to have a blue color if copper is present. Treatment of this precipitate with HCl dissolves it. Buffering is achieved with the addition of ammonia.

Confirmatory test for Mg²⁺

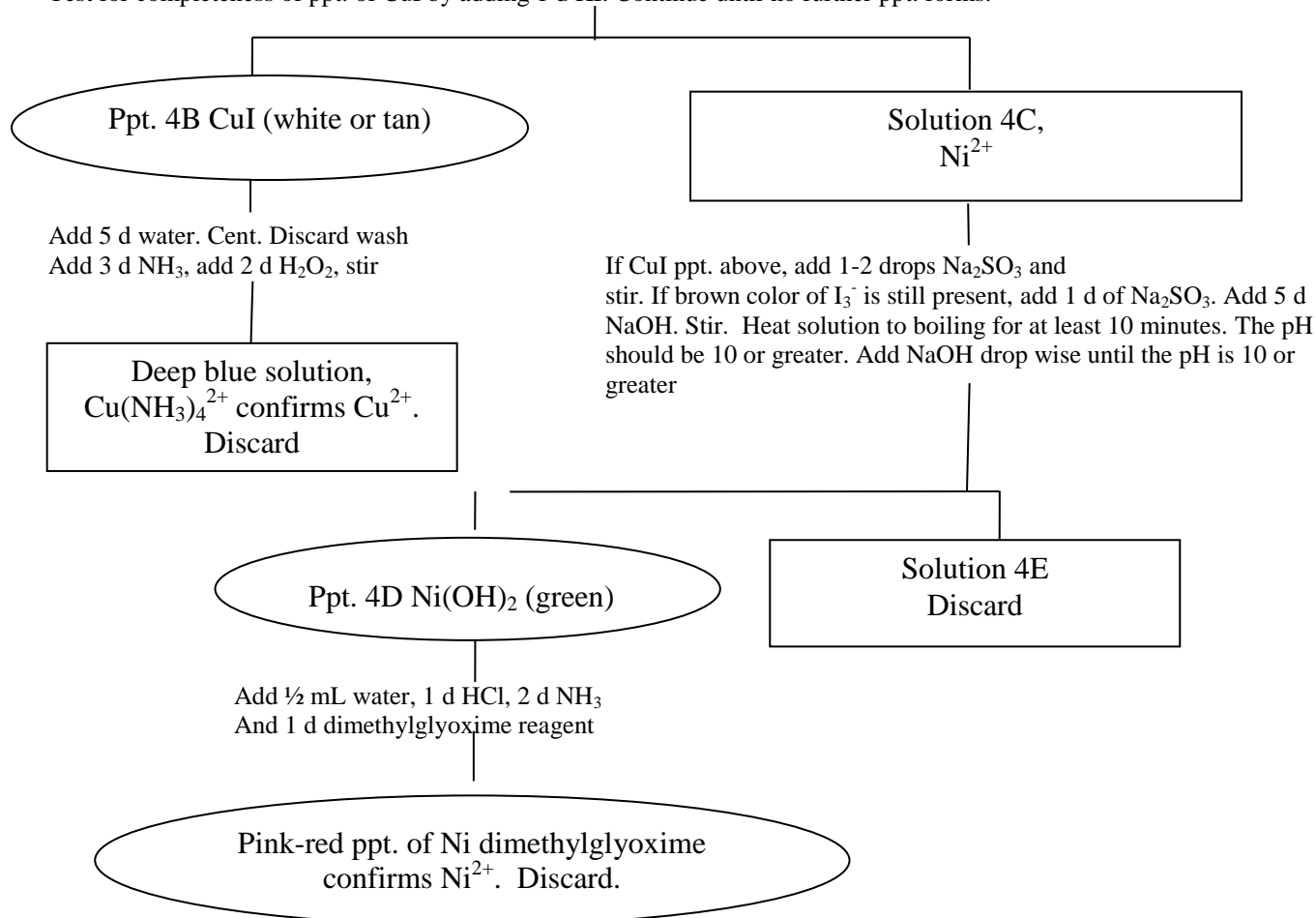
Adding the Na₂HPO₄ solution results in precipitation of white, finely divided Mg(NH₄)PO₄, confirmatory for magnesium. This process may require a minute or two to be completed.



4. Separation and Identification of the Group 4 Cations

Solution 4A from Group 3
 $\text{Cu}(\text{NH}_3)_4^{2+}$ (deep blue), $\text{Ni}(\text{NH}_3)_6^{2+}$ (light violet)

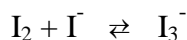
Add 6.0 M HCl until the solution is neutral (10-15 d) plus 1 d more. The solution should just turn colorless. Add 3 d KI, stir. Brown color due to I_3^- develops in addition to tan CuI ppt. If CuI is present, wait 5 minutes for ppt. to develop. Centrifuge. Test for completeness of ppt. of CuI by adding 1 d KI. Continue until no further ppt. forms.



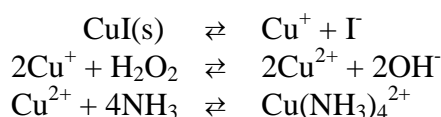
Chemical Equilibria and Reactions Involved in the Cation Scheme.

Group 4. Separation and Identification of the Copper Group

The solution remaining from the separation of Mg^{2+} contains $\text{Ni}(\text{NH}_3)_6^{2+}$ and $\text{Cu}(\text{NH}_3)_4^{2+}$. These complexes are decomposed by the addition of hydrochloric acid. The separation of copper that follows affords the opportunity of carrying out two oxidation-reduction reactions. The first is the reduction of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ using iodide, forming the insoluble tan copper (I) iodide. The brown solution that develops as the copper(I) iodide precipitates results from the formation of the very stable I_3^- complex in solution.

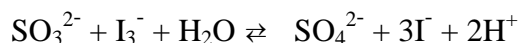


The precipitated copper(I) iodide is re-oxidized in the presence of ammonia with hydrogen peroxide, to yield the intense blue $\text{Cu}(\text{NH}_3)_4^{2+}$ in solution:

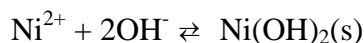


The sequence of reactions given above are a simplified view of the complex series of reactions that must occur in this case, but the net reaction is correct, production of $\text{Cu}(\text{NH}_3)_4^{2+}$ from the copper(I) iodide. The intense blue color here is a confirmatory test for copper.

In the second oxidation-reduction titration, the solution containing nickel is titrated with sodium sulfite to remove the elemental iodine produced in the precipitation of copper (I) iodide,



The end point for this reaction, at which drop wise addition of the Na_2SO_3 solution is discontinued, is indicated by the disappearance of the brown color due to the I_3^- ion. Heating the solution after adding NaOH drives off ammonia, allowing nickel to precipitate as the hydroxide.



The light green ppt. of $\text{Ni}(\text{OH})_2$ is dissolved in HCl .

The confirmatory test for Ni^{2+}

Adding dimethylglyoxime to a solution that contains Ni^{2+} forms a pink-red chelate solid.

Part 2. Anion Analysis

The cation analytical scheme outlined above is based on a systematic series of separations, followed by tests to identify individual ions once they have been isolated from the other cations in the scheme. The anion analysis is very different. In this analysis a series of tests will be carried out on each known or unknown sample. More than one anion may give a similar result in any given test, but by considering the results of all the tests, each of the anions included in the scheme for analysis can be distinguished. It may be desirable to carry out confirmatory tests for those anions that are indicated to be present by the results of the spot tests with the general reagents.

The anions included for study in this scheme are: Cl^- , Br^- , I^- , SO_3^{2-} , SO_4^{2-} , PO_4^{3-} and NO_3^- . These anions will be provided in the form of a soluble ionic solid. All of the tests, except the first one with H_2SO_4 , will be carried out on water solutions of the solids. Only a small amount of the solid is necessary to make a water solution concentrated enough to produce positive results.

Solutions need for this analysis:

H_2SO_4	18 M	$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$	0.2 M
AgNO_3	0.2 M	HCl	2.0 M
HNO_3	3.0 M	FeSO_4	0.2 M

Procedure

Week 3

The series of tests given below are to be performed using a known sample of each anion considered here. The student's observations are to be recorded in the lab notebook. Note any color changes in the solid, any gas evolution and the color and odor of the gas evolved, whether or not the solid dissolves, the color of any solution formed, etc. Direct comparisons of tests of any unknown with tests of a known sample are helpful and are encouraged.

Preparation of anion solutions. Place the amount of solid that covers approximately 1/8 of the tip of a spatula into a micro test tube and add 2-3 mL of water. If this amount of salt does not all dissolve, centrifuge and decant --using the solution and discarding the un-dissolved solid. Use portions of this solution in procedures 2 and 3.

Test

1. **Treatment with conc. H_2SO_4 .** (Safety: Concentrated H_2SO_4 is much more reactive than the dilute solutions used in the cation analysis and will cause immediate painful harm to skin tissue. Your Teaching Assistant will dispense the concentrated H_2SO_4 , but be careful not to touch it.) Place a small amount (about 1/8 inch) of the solid in a micro test tube. Add 1 to 2 d conc. H_2SO_4 (your TA will add the H_2SO_4 for you). Observe and record the results. Note color changes, bubbling, and the odor. CAUTION: Never place your nose directly over the mouth of a test tube to determine odors. Gently wave your hand over the top of the test tube, fanning any gas toward your nose. Test each of your solids in this manner and record the results in Table 2.

2. **Treatment of the solution with silver nitrate.** Place 2 d of the water solution in a micro test tube. Add 3-4 d of the 0.2 M AgNO_3 solution. Observe and record the results. If a ppt. forms, centr. and decant. Add 10 d of 3.0 M HNO_3 solution to the ppt. Stir and record any results.

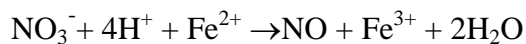
Table 2

Test 1		2		3		4
Ion Tested	Conc. H ₂ SO ₄	AgNO ₃	HNO ₃	Barium Acetate	HCl	Special
Cl ⁻						X
Br ⁻						X
I ⁻						X
SO ₃ ²⁻						X
SO ₄ ²⁻						X
PO ₄ ³⁻						X
NO ₃ ⁻						
Anion 1						
Anion 2						
Unknown Salt						

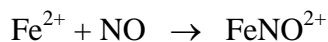
3. Treatment of the solution with barium acetate solution. Place 5 d of the solution in a micro test tube. Add 2-3 d of 0.2 M barium acetate solution. Observe and record the results. If a ppt. forms, centr. and decant. Add several drops of HCl to the solid, stir, and note any results.

Prepare solutions and test each of your solids as in 2 and 3 and record the results in Table 2.

4. Special test for nitrate anion. Since all the tests for NO₃⁻ are negative, the following positive test is recommended. Place 2 d of the solution in a micro test tube. Add carefully 10 d conc. H₂SO₄ (your TA will add the H₂SO₄ for you). Mix thoroughly and cool. Carefully add 3-4 d FeSO₄ solution, allowing the latter to float on top of the H₂SO₄ solution. Allow the tube to stand for two minutes. A brown coloration at the junction of the two layers confirms the presence of nitrate anion. The reactions that occur in this test are first reduction of NO₃⁻ to NO by Fe²⁺ at high [H⁺],



followed by formation of the brown FeNO^{2+} complex by reaction of NO with unoxidized Fe^{2+}



Analysis of Unknowns --- Carry out the above tests on each of the unknown salts. A comparison of these results with those using the known salts should indicate which anion is present in the unknown. For each unknown (labeled 1 and 2), record on Table 2, with a simple yes or no, if the result on the unknown was the same as with the known. Use this information (a series of yeses) to determine which anion is present in each of your unknowns and place the answer on the answer sheet

Part 3. Identification of an Unknown Ionic Compound

The final analysis is of a pure ionic compound to determine the identity of the cation and anion present. The samples contain two cations and one anion, each being a member of the corresponding set of ions already considered in Parts 1 and 2. All the compounds that will be analyzed are soluble in water. Preliminary observations of the solid sample should include noting its color and the pH of the solution prepared for the following analyses.

Analysis for the anion. Carry out the anion analysis just as directed in Part 2.

Analysis for the cation. Dissolve 150 to 200 mg of solid sample (a volume equal to about 2 drops of water) in 10 mL of water. Use a 1 mL portion of this solution to analyze for the cation present using the procedures given in Part 1. Record your result.

At this point, in your notebook write the formula of the compounds indicated by your anion analysis and cation analysis. Be careful to remember the charges of the ions so as to get the formula correct. Is the final result a reasonable one? Some years ago, a student reported that his water soluble unknown salt had to be AgCl. In Part 1, it has been seen that AgCl is insoluble in water.