Experiment 2-3
Qualitative Analysis of Metal Ions in Solution

Introduction

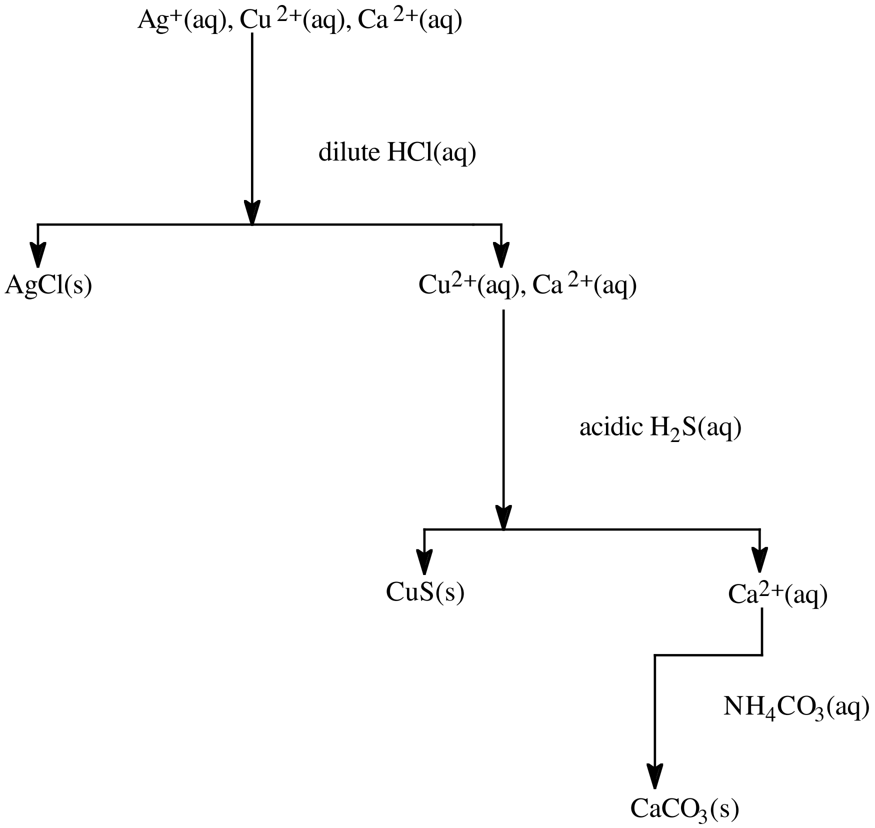
It is extremely useful to know how to detect the presence of specific ions in an aqueous solution. This type of analysis falls under the general category of analytical chemistry called ***qualitative analysis***, which addresses the question "What is in a sample?" The basis for a qualitative analysis is the fact that ions will undergo specific chemical reactions with certain reagents to yield observable products. For example, silver ion can be precipitated with hydrochloric acid to yield solid silver chloride. Because many cations will not react with hydrochloric acid in this way, this simple reaction can be used to separate ions that form insoluble chlorides from those that do not. In fact, the qualitative detection of ions in a mixture is commonly accomplished by a system of analysis in which precipitation reactions play a major role. In addition, acid-base reactions, oxidation-reduction reactions, and the formation of complex ions are often used in a systematic way for either separating ions or for determining the presence of specific ions.

The qualitative analysis of ions in a mixture must follow a scheme that can be summarized as follows: (1) Add reagents that exploit the more general properties of ions to separate major groups of ions; (2) separate major groups into subgroups with reactions that will distinguish less general properties; and (3) add reagents that will specifically confirm the presence of individual ions. Following this general three-step plan, several different analytical schemes have been devised that are based on various ways of defining major groups. In this course, you will follow a scheme which separates cations into five major groups according to the solubilities of their compounds:

Group I (Ag^+, Pb^{2+}, Hg^{2+}) cations produce insoluble chlorides so they can be precipitated with dilute HCl, while all other cations remain in solution.
Group II (Cu^{2+}, Bi^{3+}, Cd^{2+}, Hg^{2+}, As^{3+}, Sb^{3+}, Sn^{4+}) cations produce very insoluble sulfides (K_{sp} values less than 10^{-30}) so they can be precipitated by low amounts of sulfide ion; this can be achieved by adding an acidic solution of H_2S.
Group III (Al^{3+}, Cr^{3+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}) cations produce slightly soluble sulfides (K_{sp} values more than 10^{-20}) so they can be precipitated by relatively high amounts of sulfide ion; this can be achieved by adding a basic solution of H_2S.
Group IV (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) cations, as well as all of the above groups, produce insoluble carbonates so they can be precipitated by the addition of carbonate once the ions of the first three groups have been removed.
Group V (Na^+, K^+, NH_4^+) cations do not precipitate with any of the above reagents.

For a successful qualitative analysis based on the above five groups, the order of reagent addition is crucial and should follow the order listed above (that is, group I first, group II second, and so on). For example, addition of carbonate first would precipitate everything but the group V ions or addition of basic H_2S first would precipitate all group II and group III ions.

Because much of qualitative analysis involves selective precipitation and then separation of the two phases, it is convenient to represent an analytical scheme in the form of a ***flow chart***. For example, a simple flow chart is shown below for separating a known mixture of Ag^+(group I), Cu^{2+}(group II), and Ca^{2+} (group IV) ions. The addition of each reagent (presented in order from top to bottom) produces a solid phase and an aqueous phase that can be separated by centrifugation or filtration.



The above flow chart translates to the following steps: (1) add dilute HCl to precipitate AgCl from the mixture; (2) centrifuge sample to yield a solid pellet of AgCl and a ***supernatant*** (the solution that remains above the pellet after centrifugation); (3) remove the supernatant and add to it acidic H_2S to precipitate CuS; (4) centrifuge; (5) remove supernatant and add to it $NH_4CO_3(aq)$ to precipitate $CaCO_3$. Of course, this is a simplified scheme for the purpose of example; if you were to analyze an unknown mixture you would need to include: steps to check for the presence of any group III or group V ions; several steps to separate major groups into subgroups; and then confirmatory tests for the presence of each individual ion.

Once you have separated a mixture into major groups a variety of reagents can be added to distinguish subgroups or individual ions. These reagents are chosen because they react with specific ions to exploit less general properties (reactions can involve precipitation, acid-base neutralization, oxidation-reduction, or complex ion formation). In the same way that a flow chart can be used to describe the separation of major groups, you can construct flow charts for the separation of components within a major group.

In any qualitative analysis it is important to run your analytical scheme on "known" samples, prepared to contain specific ions of interest, as well as "unknown" samples in order to test your ability to use the procedure to analyze a solution of unknown composition. In this way, you can observe first-hand how a particular ion behaves when a certain reagent is added and make comparisons with the behavior of your unknown sample.

The primary objectives of this experiment are to learn how to:

- observe and record carefully the chemical behavior of ions with different reagents.
- learn how to apply fundamental chemical principles to an experimental situation.
- learn how to evaluate critically experimental observations.

General Instructions

The various reagents that you will need are either in "qual blocks" in the center of each bench, or in the hoods (solutions to be analyzed, strong bases, ammonium thiocynate) at the sides of the room. Be careful using the automatic burets and dispensers. You will work with three “known” solutions, and one “unknown.” Given the toxicity of the ions, all waste should be discarded in the appropriate waste container in the hood.

Careful notebook records should be kept of all tests on knowns and unknowns. Results in qualitative analysis are easily confused, and it is therefore very important that you be diligent about labeling your various test tubes, and that you <u>record your observations immediately</u>. It is suggested that you use the following format for your lab notebook:

Step	Substance	Reagent	Result	Inference
1.	Unknown	HCl crystals	white ppt	ions of Group I present
2.	Washed ppt from step 1	hot H_2O	ppt completely dissolves	Pb^{2+} probably present Ag^+,Hg_2^{2+} absent
3.	Solution from step 2	CH_3COOH K_2CrO_4	yellow ppt	Pb^{2+} present

General techniques in semimicro qualitative analysis

1. After adding a reagent, stir the solution thoroughly before drawing any final conclusions. This should be done whether the reaction is carried out in a centrifuge tube or a casserole. Often additional quantities of the reagent must then be added so that an excess is present.

   When the reaction is carried out in a centrifuge tube, stirring may often be carried out expeditiously, particularly if a precipitate is present originally, by bubbling air through the mixture by means of the capillary dropper or by carefully drawing the mixture up into the dropper.

2. <u>To see if precipitation is complete</u>
   a. Centrifuge and add a drop of the reagent to the clear supernatant. Observe if more precipitate is formed.

   b. Centrifuge, transfer the supernatant liquid to another centrifuge tube and add a drop of the reagent to this liquid. Centrifuge and observe if additional precipitate has formed. If the additional precipitate is very small in quantity relative to the original precipitate, it may usually be discarded. If the quantity is large, it should be combined with the original precipitate.

3. To remove the supernatant liquid from a precipitate
   Hold the centrifuge tube in the left hand in a slanting position and carefully lower the end of the dropper below the surface of the liquid so as not to disturb the precipitate. If the quantity of the liquid is large, it is usually best to remove it in several portions. Do not allow the liquid to get into the rubber bulb. Transfer the bulk of the liquid to another vessel, and then in a final operation remove the last portion of the supernatant liquid. It is often advisable to recentrifuge before removing this final portion.

4. Washing a precipitate
   After the supernatant liquid is removed, add a few drops of water or the appropriate washing solution to the precipitate and mix thoroughly, centrifuge and remove the supernatant liquid. A good general rule is to combine the liquid from the first washing with the original supernatant liquid. Repeat the washing several times, but now discard the wash water. If it is essential that the precipitate be thoroughly washed, test the washings with an appropriate reagent to see if all of the foreign ions have been removed.

5. To remove a precipitate from a centrifuge tube
   a. A portion of the precipitate may be removed by means of the stirring rod.

   b. If all of the precipitate is to be transferred to another centrifuge tube or to a casserole, this may often be accomplished by moistening it with a drop of water and sucking it up into the narrow portion of the capillary dropper. It can then be squirted into the proper vessel.

   c. If the precipitate is to be treated later with a reagent, e.g., boiled with an acid, add some of the reagent to the precipitate and mix the two together by sucking the mixture up into the dropper. The mixture is then transferred to the proper vessel by means of the dropper. Wash any remaining precipitate out with a little more of the reagent in the same way.

6. To heat a solution below its boiling point
   Put the tube in a beaker of warm or boiling water and allow it to remain there, stirring from time to time.

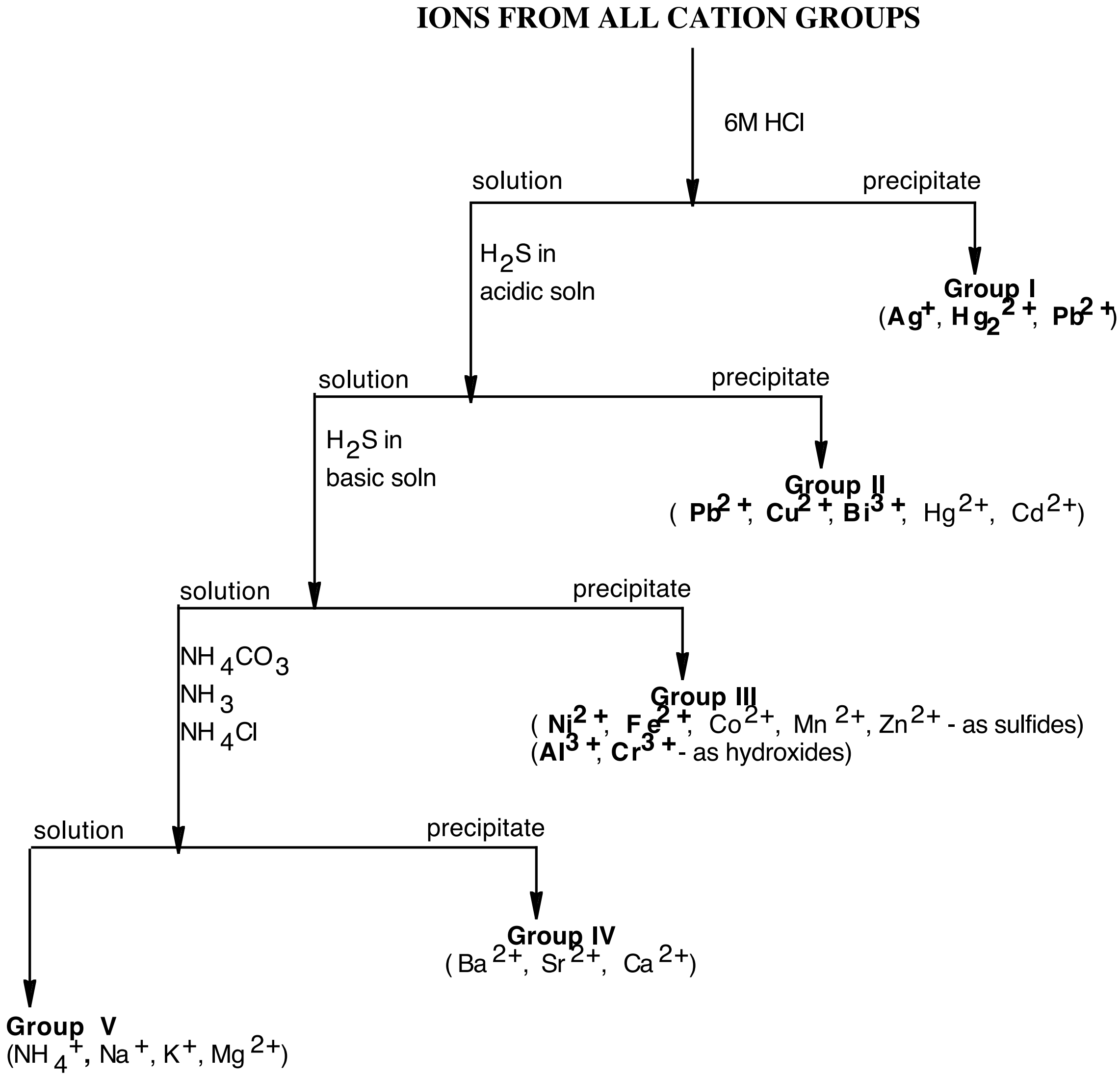
7. To evaporate a solution
   It is usually best to do this in a casserole. The casserole may be held in the hand (a rubber tube or stopper on the handle, perhaps) and is waved through the flame, or it may be put on one corner of a piece of wire gauze which is suspended well above a small flame.

   If evaporation is to be carried to dryness, at the final stage the casserole should be held in the hand so that the heating can be controlled. When only a few drops remain, tilt the casserole to one side. Remember that porcelain retains heat, so remove the casserole from the flame in plenty of time.

8. To test pH with Litmus paper
   Place a strip of litmus paper on a clean, dry surface. Place a drop of solution to be tested on the litmus paper. Use clean stirring rod to effect the transfer. Read the color of the paper while it is wet.

Overview of qualitative analysis scheme

The overall scheme for the systematic analysis of a mixtures of cations, based on the five major groups discussed above, is shown as a flow chart below. Your laboratory work will include many fewer ions (indicated in bold face type), but a number sufficient to introduce most of the principles involved.



In summary, the ions with which we will be concerned are the following:

Group I: Ag^+, Hg_2^{2+}, Pb^{2+}

Group II: Pb^{2+}, Bi^{3+}, Cu^{2+}

Group III: Ni^{2+}, Fe^{2+}, Al^{3+}, Cr^{3+}

Some relevant solubility products are:

AgCl	1.6×10^{-10}	Bi_2S_3	1.6×10^{-72}
$PbCl_2$	2.4×10^{-4}	CuS	1.0×10^{-44}
Hg_2Cl_2	1.0×10^{-18}	PbS	3.4×10^{-28}
FeS	3.7×10^{-19}	NiS	1.4×10^{-24}
$BaCO_3$	2×10^{-9}		
$Al(OH)_3$	1.8×10^{-33}		
$Cr(OH)_3$	3.0×10^{-29}	$Fe(OH)_2$	1.6×10^{-14}
$Fe(OH)_3$	1.1×10^{-36}		

where we used molar concentrations.

The remaining discussion of the qualitative analysis scheme is divided into sections according to the individual group analyses. For each group, a discussion of the chemistry involved is presented, followed by the experimental procedures for that particular group. Before beginning work on a cation group, read carefully the descriptions of the chemical reactions involved and the details of experimental procedures.

A. Group I Analysis: Pb^2, Hg_2^{2+}, Ag^+

Chemistry of the Precipitation of the Group I Cations

The precipitating reagent of Group I is a dilute solution of hydrochloric acid, and the ions precipitated are those of silver, Ag^+, mercury (I), Hg_2^{2+}, and lead (II), Pb^{2+}. The net ionic equations are:

$Ag^+ + Cl^- \rightleftharpoons AgCl(s)$ (AgCl is white, turning purple in light)

$Hg_2^{2+} + 2Cl^- \rightleftharpoons Hg_2Cl_2(s)$ (Hg_2Cl_2 is white)

$Pb^{2+} + 2Cl^- \rightleftharpoons PbCl_2(s)$ ($PbCl_2$ is white)

A slight excess of chloride ion is used to reduce the solubility of the precipitates in accordance with the common ion effect. Even so the solubility of lead chloride is sufficiently high for an appreciable concentration of lead ion to remain in solution. Most of this is precipitated with the Group II reagent.

A large excess of chloride ion should be avoided in order to prevent the formation of soluble chloro complex ions which will dissolve the precipitates:

$$AgCl + Cl^- \rightleftharpoons AgCl_2^-$$

$$PbCl_2 + Cl^- \rightleftharpoons PbCl_3^-$$

$$Hg_2Cl_2 + 2Cl^- \rightleftharpoons HgCl_4^{2-} + Hg$$

Chemistry of the Separation and Identification of the Group I Cations

The lead chloride may be extracted from the other two chlorides which may also be in the precipitate with hot water since its solubility increases with an increase in temperature much more markedly than do the solubilities of silver chloride and mercury (I) chloride.

$$PbCl_2 + H_2O \rightleftharpoons Pb^{2+}(aq) + 2Cl^-$$

The presence of lead ion is confirmed by adding an aqueous solution of potassium chromate, K_2CrO_4, which provides chromate ion to form lead chromate, $PbCrO_4$, a birght yellow solid which is less soluble than lead chloride:

$$Pb^{2+} + CrO_4^{2-} \rightleftharpoons PbCrO_4$$

The silver chloride and mercury (I) chloride which may be in the precipitate may be separated from one another by taking advantage of the fact that only silver ion forms a soluble complex ion with ammonia. By adding ammonia water to the residue, the silver chloride is selectively dissolved due to the formation of the soluble diammine silver (I) ion.

$$AgCl(s) + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$$

The addition of ammonia converts the white mercury (I) chloride in the precipitate to a mixture of white mercury (II) amidochloride and elemental mercury, black in the finely divided condition in which it is formed:

$$2NH_3 + Hg_2Cl_2(s) \rightleftharpoons HgNH_2Cl(s) + Hg(l) + NH_4^+ + Cl^-$$

The formation of the insoluble black mixture of the two principal products serves as confirming evidence for the original presence of mercury (I).
The presence of silver ion is confirmed by acidification of the solution containing the $Ag(NH_3)_2^+$ ion with nitric acid. The nitric acid converts the ammonia of the silver complex ion equilibrium to ammonium ion:

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2\,NH_3$$

$$2\,NH_3 + 2H^+ \rightleftharpoons 2NH_4^+$$

and the silver chloride reprecipitates:

$$Ag^+ + Cl^- \rightleftharpoons AgCl(s)$$

From an overall viewpoint the reaction on acidification is:

$$Ag(NH_3)_2^+ + Cl^- + 2H^+ \rightleftharpoons AgCl(s) + 2NH_4^+$$

Separation of Group I Cations

1. Use 15 drops of sample. (Throughout these instructions "one drop" refers to the amount of liquid in one drop obtained from a regular dropper, not a semimicro dropper.)

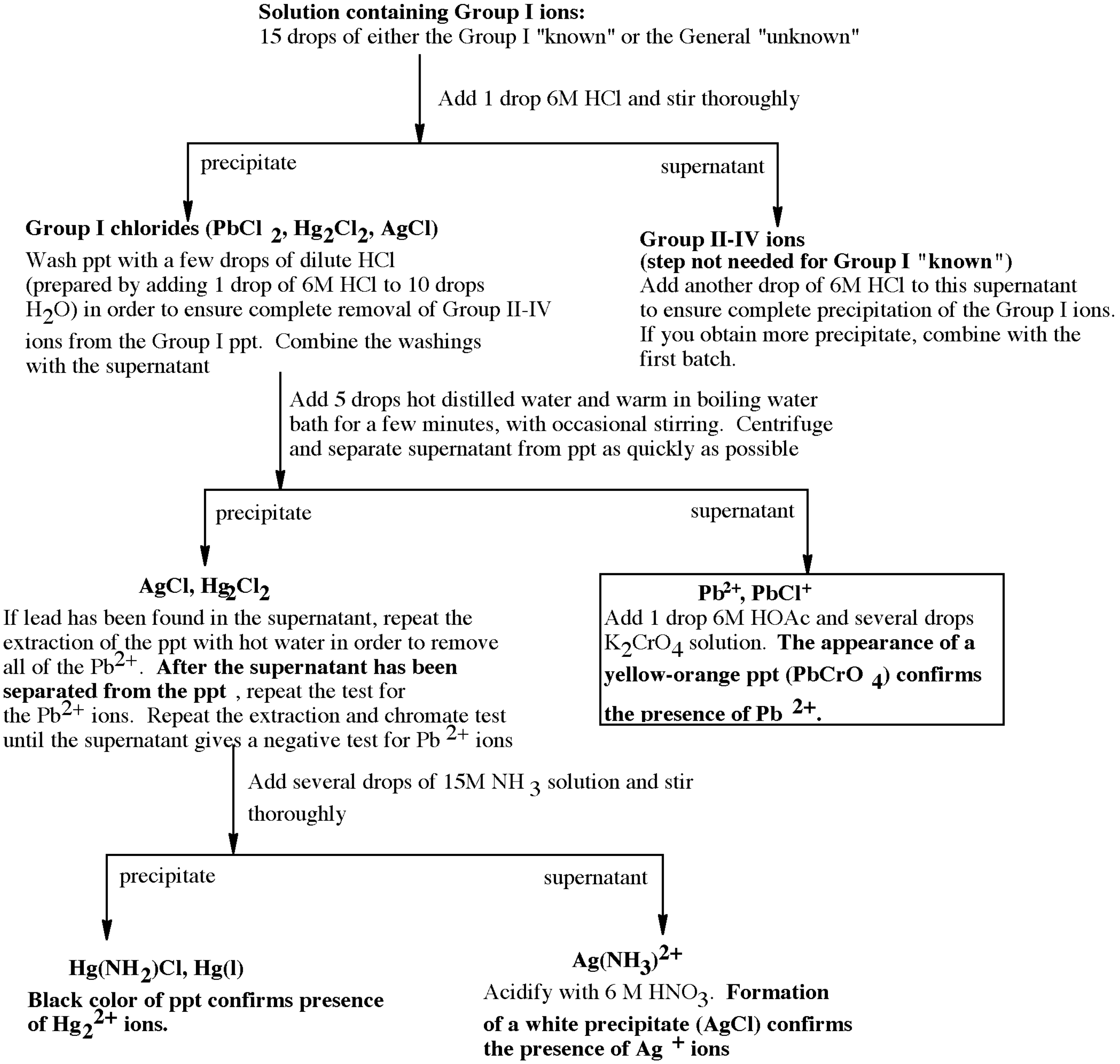
2. Precipitation of the cations of Group I as chlorides
   Add 1 drop (approx. 0.05 mL) of 6 M HCl and stir thoroughly, using a glass rod to scratch the walls of the test tube in order to induce crystallization of $PbCl_2$, which tends to stay in super-saturated solution. If a precipitate forms, centrifuge, then test for complete precipitation by adding another drop of HCl to the supernatant. Continue addition of the HCl until no more precipitation is observed, but avoid a large excess which may cause redissolving of the chlorides as complex anions.

   Stir for approximately 1 to 2 minutes to allow sufficient time for the slow precipitation of $PbCl_2$. You may want to cool the solution in an ice bath.

   Centrifuge and withdraw the supernatant as completely as possible using a semimicro dropper and transfer to another test tube. Test the transferred clear liquid for completeness of precipitation by adding 1 drop more 6 M HCl.

   Wash the precipitate with a few drops of dilute HCl (prepare by adding 1 drop of 6 M HCl to about 10 drops of water and mixing well). Discard washings.

Group I outline



Solution containing Group I ions:
15 drops of either the Group I "known" or the General "unknown"

Add 1 drop 6M HCl and stir thoroughly

Group I chlorides ($PbCl_2$, Hg_2Cl_2, AgCl)
Wash ppt with a few drops of dilute HCl (prepared by adding 1 drop of 6M HCl to 10 drops H_2O) in order to ensure complete removal of Group II-IV ions from the Group I ppt. Combine the washings with the supernatant

Group II-IV ions
(step not needed for Group I "known")
Add another drop of 6M HCl to this supernatant to ensure complete precipitation of the Group I ions. If you obtain more precipitate, combine with the first batch.

Add 5 drops hot distilled water and warm in boiling water bath for a few minutes, with occasional stirring. Centrifuge and separate supernatant from ppt as quickly as possible

AgCl, Hg_2Cl_2
If lead has been found in the supernatant, repeat the extraction of the ppt with hot water in order to remove all of the Pb^{2+}. **After the supernatant has been separated from the ppt**, repeat the test for the Pb^{2+} ions. Repeat the extraction and chromate test until the supernatant gives a negative test for Pb^{2+} ions

Pb^{2+}, $PbCl^+$
Add 1 drop 6M HOAc and several drops K_2CrO_4 solution. **The appearance of a yellow-orange ppt ($PbCrO_4$) confirms the presence of Pb^{2+}.**

Add several drops of 15M NH_3 solution and stir thoroughly

$Hg(NH_2)Cl$, Hg(l)
Black color of ppt confirms presence of Hg_2^{2+} ions.

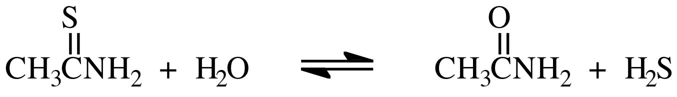
$Ag(NH_3)^{2+}$
Acidify with 6 M HNO_3. **Formation of a white precipitate (AgCl) confirms the presence of Ag^+ ions**

B. Group II Analysis: Pb^{2+}, Bi^{3+}, Cu^{2+}

Chemistry of the Precipitation of the Group II Cations

The ions of Groups II and Groups III are separated by precipitation of their insoluble sulfides. The sulfide ion is furnished by the weak electrolyte gaseous hydrogen sulfide, which is only sparingly soluble in water. At 25°C and 1 atmosphere pressure, a saturated aqueous solution contains about 0.1 mole in a liter.)

In the laboratory hydrogen sulfide is conveniently generated by hydrolyzing thioacetamide:



$$CH_3\overset{\overset{S}{\|}}{C}NH_2 + H_2O \rightleftharpoons CH_3\overset{\overset{O}{\|}}{C}NH_2 + H_2S$$

thioacetamide *acetamide*

This reaction is catalyzed by acid and is accelerated by increasing the temperature. This convenient method of generating the hydrogen sulfide is used to minimize the escape into the atmosphere of the highly toxic and unpleasant smelling gas and because it promotes the formation of purer, coarser and more easily handled sulfide precipitates.

The dissolved molecular hydrogen sulfide dissociates into hydrogen ions, hydrogen sulfide ions, HS^-, and sulfide ions, S^{2-} Three equilibria are involved:

$$H_2S(g) \rightleftharpoons H_2S(aq)$$

$$H_2S(aq) \rightleftharpoons H^+ + HS^- \qquad K_1 = \frac{[H^+][HS^-]}{[H_2S]} = 5.7\text{x}10^{-8}$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \qquad K_2 = \frac{[H^+]^2[S^{2-}]}{[HS^-]} = 1\text{x}10^{-19}$$

The low value of K_2 suggests that there is very little free S^{2-} in aqueous solutions unless they are extremely basic. Therefore, the precipitation of metal sulfides is best written

$$M^{2+} + H_2S \rightleftharpoons MS(s) + 2H^+$$

As with any equilibrium, the extent of reaction depends on the relative concentrations of products and reactants. In this case, making the solution acidic will tend to prevent precipitation of metal sulfides. The K_{sp} values given in the previous pages can be used as a general guide to the ease of precipitation of the sulfides we are using in this qualitative analysis scheme. Sulfides of very low solubility will precipitate from acidic hydrogen sulfide solutions, while sulfides of greater solubility will remain in solution and will precipitate only in basic solutions. Controlling the concentration of H^+, therefore, can be used to separate ions on this basis of differences in the solubility of their sulfides.

The ions of Group II are precipitated as their sulfides from an acidic solution of hydrogen sulfide, and for this reason Group II is often called the Acid Hydrogen Sulfide Group. The ions of Group III are precipitated as their sulfides from a basic solution of hydrogen sulfide, and Group III is often called the Basic Hydrogen Sulfide Group. If the hydrogen ion concentration is maintained in the range of 0.1 M and 0.3 M, (pH=0.5-1.0) the ions of Group II will precipitate, but not the ions of Group III, the sulfides of which are more soluble.

The reactions involved in the precipitation of Group II are as follows (for the ions we are considering):

$Pb^{+2} + H_2S \rightleftharpoons PbS(s) + 2H^+$ (PbS is black)

$2Bi^{+3} + 3H_2S \rightleftharpoons Bi_2S_3(s) + 6H^+$ (Bi_2S_3 is brown)

$Cu^{+2} + H_2S \rightleftharpoons CuS(s) + 2H^+$ (CuS is black)

Chemistry of the Separation and Identification of the Group II Cations

The first step involves the conversion of the sulfides of the precipitate to soluble nitrates by treatment with nitric acid. The reactions involved are as follows:

$$PbS(s) + 2NO_3^-(aq) + 4H^+(aq) \rightleftharpoons Pb^{2+}(aq) + S(s) + 2NO_2\,(g) + 2H_2O$$

$$CuS(s) + 2NO_3^-(aq) + 4H^+\,(aq) \rightleftharpoons Cu^{2+}\,(aq) + S(s) + 2NO_2\,(g) + 2H_2O$$

$$Bi_2S_3\,(s) + 6NO_3^-(aq) + 12H^+\,(aq) \rightleftharpoons 2Bi^{3+}(aq) + 3S(s) + 6NO_2\,(g) + 6H_2O$$

The Pb^{2+} ion is separated from the soluble mixture by conversion to its insoluble sulfate:

$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4\,(s)$ ($PbSO_4$ is white)

The sulfate ions are provided by the addition of sulfuric acid. To make the precipitation as complete as possible, the nitric acid must be removed because the nitrate ions tend to dissolve the lead sulfate because of the following reaction:

$$Pb^{2+} + NO_3^- \rightleftharpoons PbNO_3^+$$

And the hydrogen ions also tend to dissolve the lead sulfate because of their action on the sulfate ions:

$$H^+ + PbSO_4 \rightleftharpoons Pb^{2+} + HSO_4^-$$

The nitric acid is removed by heating the reaction mixture. As the sulfuric acid is concentrated, it converts the nitrate ion into molecular nitric acid which is then removed by evaporation.

$$NO_3^- + H_2SO_4 \rightleftharpoons HNO_3\,(g) + HSO_4^-$$

When the nitric acid has been removed the temperature increases, further bringing about the decomposition of the sulfuric acid:

$$H_2SO_4 \rightleftharpoons SO_3\,(g) + H_2O(g)$$

The sulfur trioxide forms dense white fumes, the appearance of which indicates the removal of the nitric acid and its solubilizing influence. Do not evaporate to dryness. Note: This step is very important; if not done correctly, Pb^{2+-} will be carried over and give false tests for other ions.

The insoluble lead sulfate is dissolved by the addition of acetate ion as ammonium acetate to form a complex ion:

$$PbSO_4\,(s) + 3CH_3COO^- \rightleftharpoons Pb(CH_3COO)_3^- + SO_4^{2-}$$

The addition of chromate ion in the form of potassium chromate precipitates the lead ion as the orange yellow lead chromate which confirms the presence of lead ion.

$$Pb(CH_3COO)_3^- + CrO_4^{2-} \rightleftharpoons PbCrO_4\,(s) + 3CH_3COO^-$$

The supernatant remaining from the precipitation of lead sulfate possibly contains both bismuth III and copper II ions. The bismuth III ions are separated by precipitation as white gelatinous bismuth (III) hydroxide upon the addition of an aqueous solution of ammonia:

$$Bi^{3+} + 3NH_3 + 3H_2O \rightleftharpoons Bi(OH)_3\,(s) + 3NH_4^+$$

The presence of bismuth III ion is confirmed by converting the white bismuth (III) hydroxide to jet black, finely divided elemental bismuth through the addition of stannite ion, $Sn(OH)_3^-$ as sodium stannite, $NaSn(OH)_3$.

$$3OH^- + 2Bi(OH)_3\,(s) + 3Sn(OH)_3^- \rightleftharpoons 3Sn(OH)_6^{2-} + 2Bi(s) \qquad \text{(Bi is black)}$$

The sodium stannite solution is prepared by adding sodium hydroxide to a solution of tin (II) chloride until the precipitate of tin (II) hydroxide, formed at first, dissolves. The reactions are:

$$2NaOH + SnCl_2 \rightleftharpoons Sn(OH)_2\,(s) + 2NaCl$$

$$Sn(OH)_2\,(s) + NaOH \rightleftharpoons NaSn(OH)_3$$

The addition of the ammonia water to precipitate the bismuth hydroxide also converts any copper II ion present to the deep blue complex ion, $Cu(NH_2)^{2+}$.

$$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+} \qquad (Cu(NH_3)_4^{2+} \text{ is deep blue})$$

The occurrence of the deep blue solution confirms the presence of copper II ion.

Separation of Group II Cations

1. Calibration of a test tube
   Measure 2.5 mL of water with the 10 mL graduate cylinder into a small dry test tube and mark the water level using a file.

2. Adjustment of the acidity and precipitation of the cations of Group II using thioacetamide.
   (a) Place 15 drops of the Group II known solution (or all of Group I supernatant if working on general unknown) containing the cations in the calibrated tube and add 6 M ammonia solution drop-wise with good stirring until the solution is basic (test with red litmus paper). If an analysis of all groups is being made, use all of the supernatant from the first Group I precipitation and make basic with 6 M ammonia solution as above.

   Add 2 M HCl (which you have prepared from 6 M HCl) carefully, with good stirring, until the pH is between 2 and 3 (short range indicator paper). If the solution becomes too acid, add a fraction of a drop of 6 M NH_3 solution (from a stirring rod) to achieve range.

   Add 0.35 mL (7 drops) more 2 M HCl. Then add 4 drops of 11% thioacetamide solution (TA), make up to the mark at 2.5 mL with water, and mix well. At this point the pH should be approximately 0.5 (corresponding to a hydrogen ion concentration of 0.3 M).

   (b) Heat the solution in a bath of boiling water for 5 minutes. Centrifuge, withdraw the supernatant to another test tube. Check the acidity of the solution with short range test paper and, if necessary, add sufficient 6 M NH_3 solution to raise the pH to 0.5 again.

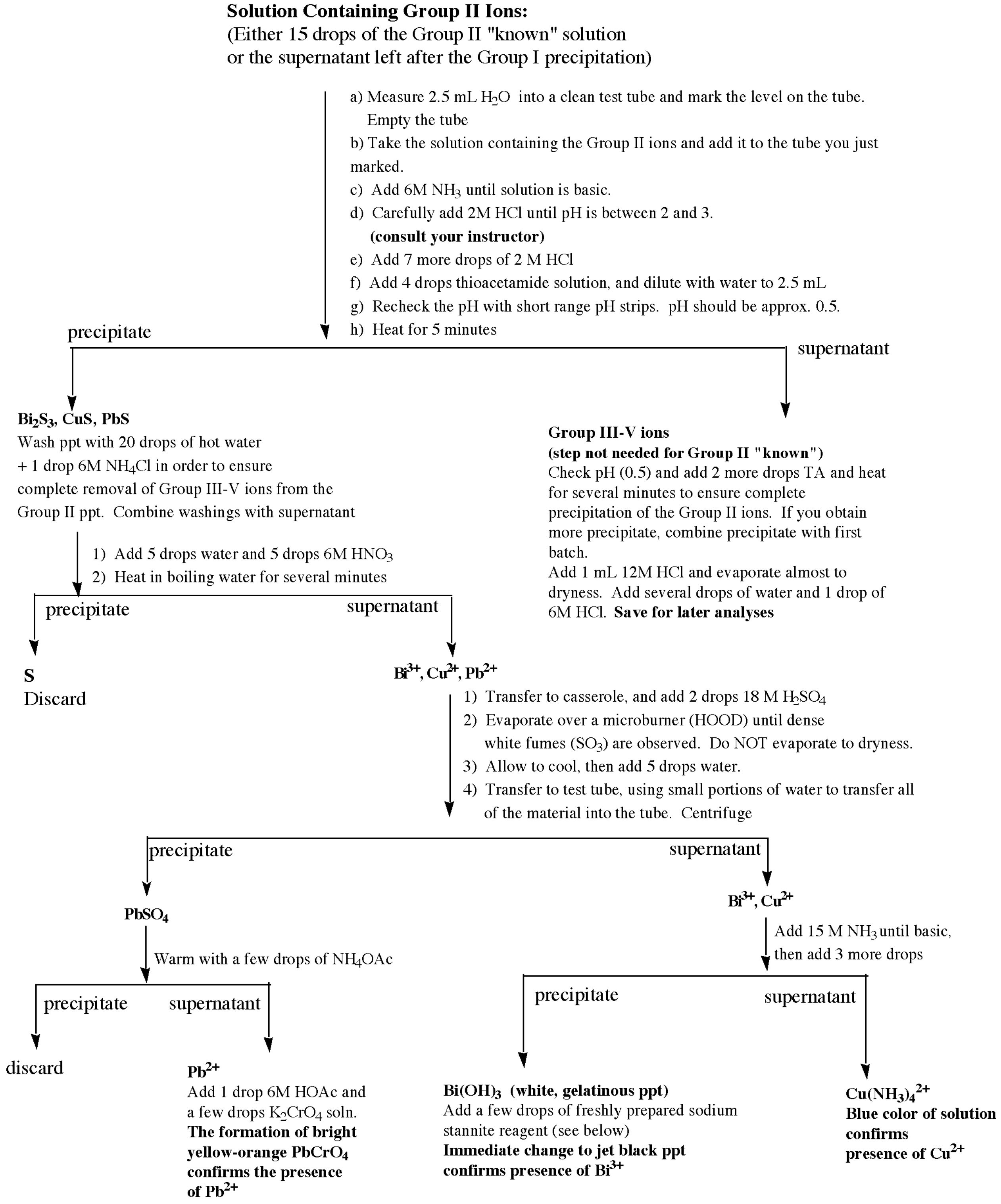
   (c) Add 2 additional drops TA reagent and heat for several minutes in the boiling water. Centrifuge if more precipitate appears and continue heating and centrifuging as long as a precipitate is obtained.

   At this stage you will have a precipitate (one or more portions) containing the sulfides of Pb^{2+}, Cu^{2+} and Bi^{3+} as well as a clear liquid supernatant containing the cations of later Groups, if present.

   (d) Treatment of the precipitate of Group II sulfides
   Combine the portions of the sulfide precipitate and wash the precipitate twice, each time with approximately 20 drops of hot water containing 1 drop of 6 M NH_4Cl. Add the first washings to the clear supernatant containing the cations of later Groups. Discard the second washings. If doing only Group II analysis, discard the supernatant and both washings.

   (e) If you are to analyze for cations in later Groups, add 1 ml 12 M HCl to the combined solutions (clear supernatant from Group II sulfides plus first washings), transfer to a casserole and evaporate almost to dryness (**CARE**). Then add several drops water and 1 drop 6 M HCl and reserve for Group III analysis.

Group II Outline



Solution Containing Group II Ions:
(Either 15 drops of the Group II "known" solution
or the supernatant left after the Group I precipitation)

a) Measure 2.5 mL H_2O into a clean test tube and mark the level on the tube. Empty the tube
b) Take the solution containing the Group II ions and add it to the tube you just marked.
c) Add 6M NH_3 until solution is basic.
d) Carefully add 2M HCl until pH is between 2 and 3. **(consult your instructor)**
e) Add 7 more drops of 2 M HCl
f) Add 4 drops thioacetamide solution, and dilute with water to 2.5 mL
g) Recheck the pH with short range pH strips. pH should be approx. 0.5.
h) Heat for 5 minutes

precipitate

Bi_2S_3, CuS, PbS
Wash ppt with 20 drops of hot water + 1 drop 6M NH_4Cl in order to ensure complete removal of Group III-V ions from the Group II ppt. Combine washings with supernatant

1) Add 5 drops water and 5 drops 6M HNO_3
2) Heat in boiling water for several minutes

precipitate

S
Discard

supernatant

Bi^{3+}, Cu^{2+}, Pb^{2+}

1) Transfer to casserole, and add 2 drops 18 M H_2SO_4
2) Evaporate over a microburner (HOOD) until dense white fumes (SO_3) are observed. Do NOT evaporate to dryness.
3) Allow to cool, then add 5 drops water.
4) Transfer to test tube, using small portions of water to transfer all of the material into the tube. Centrifuge

precipitate

$PbSO_4$

Warm with a few drops of NH_4OAc

precipitate

discard

supernatant

Pb^{2+}
Add 1 drop 6M HOAc and a few drops K_2CrO_4 soln.
The formation of bright yellow-orange $PbCrO_4$ confirms the presence of Pb^{2+}

supernatant

Bi^{3+}, Cu^{2+}

Add 15 M NH_3 until basic, then add 3 more drops

precipitate

$Bi(OH)_3$ (white, gelatinous ppt)
Add a few drops of freshly prepared sodium stannite reagent (see below)
Immediate change to jet black ppt confirms presence of Bi^{3+}

supernatant

$Cu(NH_3)_4^{2+}$
Blue color of solution confirms presence of Cu^{2+}

supernatant

Group III-V ions
(step not needed for Group II "known")
Check pH (0.5) and add 2 more drops TA and heat for several minutes to ensure complete precipitation of the Group II ions. If you obtain more precipitate, combine precipitate with first batch.
Add 1 mL 12M HCl and evaporate almost to dryness. Add several drops of water and 1 drop of 6M HCl. **Save for later analyses**

Preparation of sodium stannite reagent:
Place 1 drop of SnCl2 solution in a test tube.
Add 6 M NaOH drop by drop until the $Sn(OH)_2$ ppt which initially forms redissolves.

C. Group III Analysis: Ni^{2+}, Fe^{2+}, Al^{3+}, Cr^{3+}

The Chemistry of the Precipitation of the Group III Cations

The ions of Group III are precipitated as their sulfides, or as their hydroxides, from a basic solution of hydrogen sulfide. The sulfides of the ions of Group III are not sufficiently insoluble to be precipitated in the acidic solution of hydrogen sulfide of Group II but will be precipitated by basic solutions of hydrogen sulfide.

A basic hydrogen sulfide solution also contains a concentration of hydroxide ions. Although this is very small, it is sufficient to precipitate the very insoluble hydroxides of aluminum and chromium (III) ions. The equations for the precipitation of the ions of Group III under consideration in our laboratory work are:

$Ni^{2+} + H_2S \rightleftharpoons NiS(s) + 2H^+$ (NiS is black)

$Fe^{2+} + H_2S \rightleftharpoons FeS(s) + 2H^+$ (FeS is black)

$Al^{3+} + 3NH_3 + 3H_2O \rightleftharpoons Al(OH)_3(s) + 3NH_4^+$ ($Al(OH)_3$ is white, gelatinous)

$Cr^{3+} + 3NH_3 + 3H_2O \rightleftharpoons Cr(OH)_3(s) + 3NH_4^+$ ($Cr(OH)_3$ is gray-green, gelatinous)

Care must be taken not to have the solution of hydrogen sulfide too basic, for if the concentration of hydroxide ion is sufficiently high, unwanted precipitation of magnesium hydroxide will take place. To achieve a hydroxide ion concentration of the necessary concentration (about 1×10^{-5} M) an ammonia-ammonium chloride buffer is produced by adding ammonia to a solution of ammonium chloride.

In the ammonia solution the following ionization equilibrium prevails:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The hydroxide ion concentration of a 0.1 M NH_3 solution is about 1.3×10^{-3} M which is sufficiently high to precipitate magnesium hydroxide. The presence of the added ammonium ion concentration from the ammonium chloride displaces the ammonia equilibrium to the left (common ion effect) reducing the hydroxide ion concentration. In practice sufficient ammonium chloride is added to reduce the hydroxide ion concentration to about 1×10^{-5} M. A hydroxide concentration of this value is sufficient to precipitate the slightly soluble aluminum and chromium hydroxides but not the more soluble magnesium hydroxide (compare the K_{sp} values of the hydroxides).

In the course of producing the ammonia-ammonium chloride buffer (before the thioacetamide solution is added), the following reactions will take place if the appropriate ions are present:

$$Ni^{2+}\ \text{(green)} + 6NH_3 \rightleftharpoons Ni(NH_3)_6^{2+}\ \text{(blue)}$$

$$Fe^{3+} + 3NH_3 + 3H_2O \rightleftharpoons Fe(OH)_3\,(s) + 3NH_4^+ \quad \text{(}Fe(OH)_3\text{ is reddish brown)}$$

$$Al^{3+} + 3NH_3 + 3H_2O \rightleftharpoons Al(OH)_3\,(s) + 3NH_4^+ \quad \text{(}Al(OH)_3\text{ is white, gelatinous)}$$

$$Cr^{3+} + 3NH_3 + 3H_2O \rightleftharpoons Cr(OH)_3\,(s) + 3NH_4^+ \quad \text{(}Cr(OH)_3\text{ is gray-green, gelatinous)}$$

The hydrogen sulfide for the precipitation in the basic solution is generated by the hydrolysis of thioacetamide as in the acidic solution of Group II, but in basic solution the hydrolysis reaction is much more complex and less well understood.

> (Note: As handed out, Group III knowns and unknowns contain Fe^{3+}, which is reduced by H_2S and forms FeS. If Fe^{2+} were present, it would also precipitate as a greenish gelatinous hydroxide.)

Chemistry of the Separation and Identification of the Group III Cations

The group precipitate containing nickel (II) sulfide, iron (II) sulfide, aluminum hydroxide, and chromium hydroxide is dissolved by heating in a dilute solution of nitric acid. The reactions are:

$$Cr(OH)_3(s) + 3H^+ \rightleftharpoons Cr^{3+} + 3H_2O$$

$$Al(OH)_3\,(s) + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$$

$$NiS(s) + 2NO_3^- + 4H^+ \rightleftharpoons Ni^{2+} + S + 2NO_2(g) + 2H_2O$$

$$FeS(s) + 3NO_3^- + 6H^+ \rightleftharpoons Fe^{3+} + S + 3NO_2\,(g) + 3H_2O$$

Note that in this process Fe^{2+} ions are oxidized to Fe^{3+} ions.

The iron (III) and Ni (II) are separated as hydroxides by precipitation with an excess of sodium hydroxide in the presence of hydrogen peroxide.

$$Ni^{2+} + 2OH^- \rightleftharpoons Ni(OH)_2\,(s)\ \text{(green)}$$

$$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_3(s)\ \text{(red-brown)}$$

The amphoteric aluminum hydroxide is converted to the tetrahydroxo-aluminate complex by the hydroxide ion:

$$Al^{3+} + 3OH^- \rightleftharpoons Al(OH)_3\,(s)$$

$$Al(OH)_3\,(s) + OH^- \rightleftharpoons Al(OH)_4^-$$

The chromium ion is oxidized by hydrogen peroxide in the basic solution to yellow chromate ion by the following reaction:

$$2Cr^{3+} + 3H_2O_2 + 10\,OH^- \rightleftharpoons 2CrO_4^{2-} + 8H_2O \quad (CrO_4^{2-}\text{ is yellow})$$

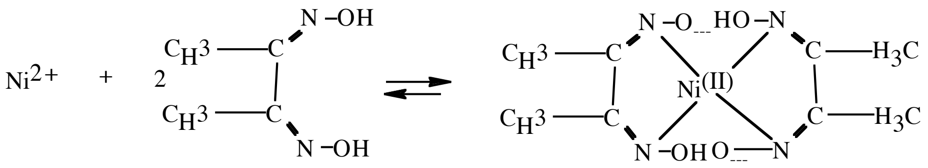
The precipitates of nickel (II) hydroxide and iron (III) hydroxide are removed by centrifugation and redissolved by treatment with hydrochloric acid.

$$Fe(OH)_3 + 3H^+ \rightleftharpoons Fe^{3+} + 3H_2O$$

$$Ni(OH)_2 + 2H^+ \rightleftharpoons Ni^{2+} + 2H_2O$$

The presence of iron (III) ion is confirmed by the appearance of the characteristic deep red color of the thiocyanate complex ion on addition of ammonium thiocyanate:

$$Fe^{3+} + SCN^- \rightleftharpoons Fe(SCN)^{2+} \qquad \text{(deep red)}$$



dimethylglyoxime (dmg)

nickel(dmg) 2

The presence of nickel is confirmed by converting the Ni (II) ion to a scarlet red complex with dimethylglyoxime.

The nickel dimethylglyoxime is a special type of complex in which the complexing agent bonds with the ion at more than one coordinating position. Such a complex is designated with the special name chelate, and the phenomenon is called chelation.

In order to avoid the possibility of obscuring the formation of the scarlet nickel dimethylglyoxime precipitate, the reaction solution is first treated with ammonia water to precipitate any iron (III) ion as iron (III) hydroxide.

$$Fe^{3+} + 3NH_3 + 3H_2O \rightleftharpoons Fe(OH)_3\,(s) + 3NH_4^+$$

The relatively small concentration of the hydroxide ion furnished by the weakly dissociated ammonia water is sufficient to precipitate the very slightly soluble iron (III) hydroxide without precipitating the more soluble nickel (II) hydroxide (compare the solubility product constants).

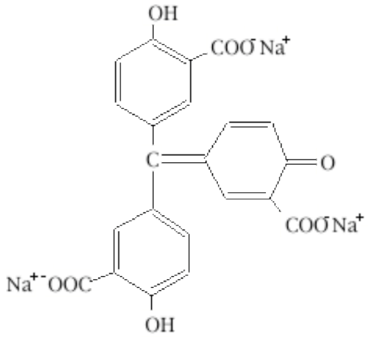
The presence of chromate ion is suggested if the supernatant from the treatment with the sodium hydroxide is yellow. The presence of chromate ion is confirmed by precipitation of yellow lead chromate from a weakly acid solution on addition of lead acetate:

$$Pb^{2+} + CrO_4^{2-} \rightleftharpoons PbCrO_4(s) \quad \text{(yellow)}$$

The presence of aluminum ion is detected by precipitation of the white, gelatinous aluminum hydroxide; confirmation involves dissolving this precipitate and reprecipitating in the presence of a red dye called aluminon. The aluminum hydroxide absorbs the red dye to form what is known as a "lake". The precipitation of aluminum hydroxide is carried out with ammonia to avoid the possibility of converting the aluminum hydroxide to aluminate ion. The precipitation reaction is:

$$Al^{3+} + 3NH_3 + 3H_2O \rightleftharpoons 3NH_4^+ + Al(OH)_3\,(s) \qquad \text{(white, gelatinous)}$$

The structure of the aluminon is:



Separation of Group III Cations

1. Use 15 drops of the Group III known or unknown solution. If an analysis of all groups is being made, use all of the supernatant from the initial precipitation of Group II, the liquid from 2(e), Group II.

2. Dilute the sample or liquid from 2(e) Group with water to a total volume of approximately 2 ml.

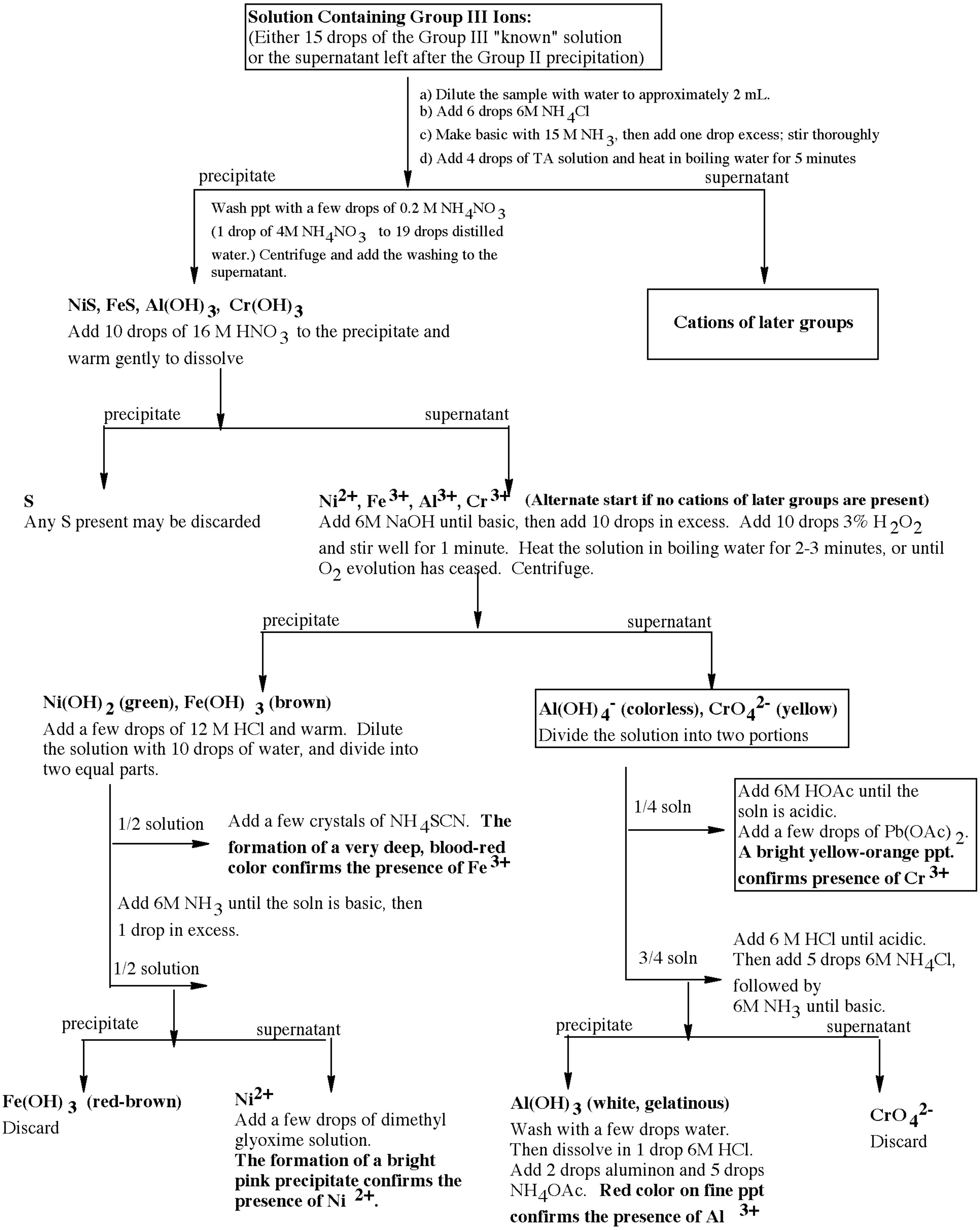
3. Add 6 drops 6 M NH_4Cl and make the solution basic with 15 M NH_3 (test with litmus), using 1 drop of 15 M NH_3 in excess. Shake for several minutes with free access to air.

   At this point note carefully whether or not a precipitate is present. A colored solution often obscures a precipitate. Record the color and appearance of any precipitate.

   Add 4 drops of TA solution and heat in the boiling water bath for at least five minutes.

   Centrifuge.

Group III Outline



Solution Containing Group III Ions:
(Either 15 drops of the Group III "known" solution
or the supernatant left after the Group II precipitation)

a) Dilute the sample with water to approximately 2 mL.
b) Add 6 drops 6M NH_4Cl
c) Make basic with 15 M NH_3, then add one drop excess; stir thoroughly
d) Add 4 drops of TA solution and heat in boiling water for 5 minutes

precipitate

Wash ppt with a few drops of 0.2 M NH_4NO_3 (1 drop of 4M NH_4NO_3 to 19 drops distilled water.) Centrifuge and add the washing to the supernatant.

NiS, FeS, $Al(OH)_3$, $Cr(OH)_3$
Add 10 drops of 16 M HNO_3 to the precipitate and warm gently to dissolve

precipitate

S
Any S present may be discarded

supernatant

Ni^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+} **(Alternate start if no cations of later groups are present)**
Add 6M NaOH until basic, then add 10 drops in excess. Add 10 drops 3% H_2O_2 and stir well for 1 minute. Heat the solution in boiling water for 2-3 minutes, or until O_2 evolution has ceased. Centrifuge.

precipitate

$Ni(OH)_2$ (green), $Fe(OH)_3$ (brown)
Add a few drops of 12 M HCl and warm. Dilute the solution with 10 drops of water, and divide into two equal parts.

1/2 solution

Add a few crystals of NH_4SCN. **The formation of a very deep, blood-red color confirms the presence of Fe^{3+}**

Add 6M NH_3 until the soln is basic, then 1 drop in excess.

1/2 solution

precipitate

$Fe(OH)_3$ (red-brown)
Discard

supernatant

Ni^{2+}
Add a few drops of dimethyl glyoxime solution.
The formation of a bright pink precipitate confirms the presence of Ni^{2+}.

supernatant

$Al(OH)_4^-$ (colorless), CrO_4^{2-} (yellow)
Divide the solution into two portions

1/4 soln

Add 6M HOAc until the soln is acidic.
Add a few drops of $Pb(OAc)_2$.
A bright yellow-orange ppt. confirms presence of Cr^{3+}

3/4 soln

Add 6 M HCl until acidic.
Then add 5 drops 6M NH_4Cl, followed by 6M NH_3 until basic.

precipitate

$Al(OH)_3$ (white, gelatinous)
Wash with a few drops water.
Then dissolve in 1 drop 6M HCl.
Add 2 drops aluminon and 5 drops NH_4OAc. **Red color on fine ppt confirms the presence of Al^{3+}**

supernatant

CrO_4^{2-}
Discard

supernatant

Cations of later groups

Experiment 2-3 Worksheet — Qualitative Analysis Results

Name: ______________________________ Date of Experiment: _____________

Date of Report: _________________

<u>Experimental Results</u>

Ions Present ______________________

Write up (no more than 2-4 pages) a summary of how you arrived at the identification of ions in your unknown solution. Make sure to separate your observations from your inference/conclusion. You should present this in as organized and clear a fashion as possible – give some thought to how best to do this and consult the introductory section of this manual (page 21). Include chemical reactions only for those ions that were present in your solution – that is, to describe reactions that actually occurred in your sample, rather than all that could have occurred. Discuss any possible uncertainties in your conclusion.