

Experiment 7

Qualitative Analysis of Group I Cations- The Silver Group

Pre-Lab Assignment

Before coming to lab:

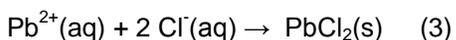
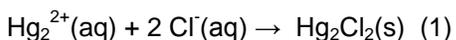
- Read the lab thoroughly.
- Answer the pre-lab questions that appear at the end of this lab exercise. The questions should be answered on a separate (new) page of your lab notebook. Be sure to show all work, round answers, and include units on all answers.
- Follow the guidelines in the "Lab Notebook Policy and Format for Lab Reports" section of the lab manual to complete in your lab notebook the following sections of the report for this lab exercise: Title, Lab Purpose, and Procedure and Data Tables. Your Data Table section will include a flow chart that summarizes the directions and results of the experiment.

Purpose

In this lab, you will gain experience with qualitative analysis by identifying whether an unknown sample contains Ag^+ , Hg^{2+} and/or Pb^{2+} .

Background

Qualitative analysis is a branch of analytical chemistry that identifies particular substances in a given sample of material. In this experiment, you will analyze a known solution that contains all the Group I cations—silver, lead, and mercury(I)—and an unknown solution to determine which of these ions are present and which are absent. These three cations are grouped together because they are the only common cations that form insoluble precipitates when reacted with chloride. Therefore, they can be removed as a group from solution by the addition of HCl. The reactions that occur are simple precipitations and can be represented by the equations:



It is important to add enough HCl to ensure complete precipitation but not too large an excess. In concentrated HCl solution, these chlorides tend to dissolve producing soluble chloro-complexes such as AgCl_2^- (aq) and PbCl_4^{2-} (aq).

<u>K_{sp} of Group I Chlorides at 25 °C</u>	
Hg ₂ Cl ₂	1.1 x 10 ⁻¹⁸
AgCl	1.8 x 10 ⁻¹⁰
PbCl ₂	1.7 x 10 ⁻⁵

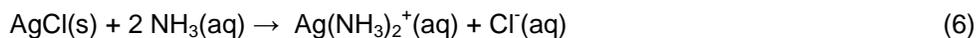
Referring to the K_{sp} values of AgCl and PbCl₂, note that PbCl₂ is significantly more soluble than AgCl and Hg₂Cl₂. In addition, the solubility of PbCl₂ increases approximately threefold as the temperature of the solution increases from 20°C to 100°C. The solubilities of AgCl and Hg₂Cl₂ increases very little over this temperature range. Thus, PbCl₂ can be separated from the other two chlorides by adding hot water. In hot water, PbCl₂ will dissolve while AgCl and Hg₂Cl₂ remains insoluble.



Once Pb^{2+} has been put into solution, we can check for its presence by adding a solution of K_2CrO_4 . The chromate ion, CrO_4^{2-} , gives a yellow precipitate with Pb^{2+} :



The other two insoluble chlorides, AgCl and Hg_2Cl_2 , can be separated by adding aqueous ammonia. Silver chloride dissolves, forming the soluble complex ion $\text{Ag}(\text{NH}_3)_2^+$:

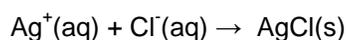
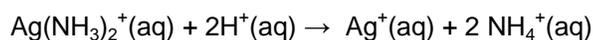


Ammonia also reacts with Hg_2Cl_2 via a rather unusual oxidation-reduction reaction. The products include finely divided metallic mercury, which is black, and a compound with formula HgNH_2Cl , which is white:



As this reaction occurs, the solid appears to change color, from white to black or grey which indicates the presence of mercury.

To establish the presence of silver, the solution containing $\text{Ag}(\text{NH}_3)_2^+$ needs to be further tested. The addition of a strong acid (HNO_3) to the solution destroys the complex ion and re-precipitates silver chloride. We may consider that this reaction occurs in two steps:



The formation of a white precipitate indicates the presence of silver in the solution.

Laboratory Techniques used in Inorganic Qualitative Analysis

Attention to detail is critical when performing qualitative analysis experiments. Below are some general guidelines to help you get excellent results.

Cleanliness

Make sure that all test tubes and stirring rods are clean. Rinse the test tubes with deionized water and shake off as much of the liquid as possible before use. Rinse stirring rods before using them. Rinse droppers before reusing them for a different solution.

Adding Reagents

Use clean droppers. Some liquid reagents may be dispensed from bottles equipped with dropper caps. **Be sure to replace the cap on the correct bottle.** Failure to do so may ruin not only your lab, but other students' labs as well. Screw the cap on firmly if it is a screw cap. Never place the tip of a dispensing dropper into your test solution in the test tube. Insert the tip about 0.5 cm below the top of the test tube, and release the indicated number of drops.

Mixing

If a small amount of liquid is present in a test tube, it may be mixed by flicking the base of the test tube with a finger while holding the test tube lightly by the top. Never shake a test tube that is capped with a finger or cork. Getting chemicals on fingers is an excellent means of introducing them into your body. Even if gloves are used, using a finger to cap a test tube is an easy means of contaminating other solutions. Also, if a test tube is capped with a finger or a cork, pressure may build up due to the evolution of heat or a gas in the test tube. Pressure build up can cause chemicals to spray out of the test tube. If the flicking technique is unsuccessful, or if the test tube is more than one-third full, a glass stirring rod should be used to mix the contents. Unless otherwise directed, always mix thoroughly after adding each reagent before making observations, checking pH or proceeding to the next step.

Centrifuging

Be sure that the test tubes in use are the appropriate size for the centrifuge. A tube of approximately the same mass in the opposite slot of the centrifuge must be used to balance the centrifuge. This is easily accomplished by using a test tube of the same size which is filled to approximately the same height with water. If you are simultaneously testing a known and an unknown, they can usually be used to balance each other. Other test tubes in the centrifuge may be of different masses, but each opposite pair should be matched. If the centrifuge is too unbalanced, it may "walk" around the countertop while it is spinning. Be sure that test tubes being centrifuged are neither cracked nor chipped. The stress applied by the centrifuge can cause damaged test tubes to shatter, resulting in chemicals and pieces of glass being scattered inside the centrifuge. Long hair must be tied back to avoid tangling in the centrifuge.

Decanting

After centrifuging, the supernatant (the liquid above a precipitate, also called the decantate), is usually decanted into a clean test tube. Carefully tip the test tube and pour off the supernatant without disturbing solid. It may be poured directly or a stirring rod may be placed across the mouth of the test tube to direct the supernatant into a clean test tube.

Washing a Precipitate

After separation from the supernatant, a precipitate is often washed to free it from reagents that might interfere at a later stage. Usually the rinse is deionized water, but other liquids or solutions may be used. Add the indicated amount of the wash liquid and stir the contents of the test tube thoroughly. The pellet of solid must be broken up and mixed well with the wash liquid. After thorough stirring, centrifuge the sample and decant the wash solution.

Heating

Due to the small quantity of material being heated, test tubes containing samples should NEVER be heated directly in a flame. A solution in test tube can reach its boiling point within a few seconds, and may be ejected violently from the test tube. All heating should be done using a water bath on a hot plate. Be careful that the tops of the test tubes are well above the water. The water may be boiling at times and could spatter into the test tubes, contaminating the contents.

Testing pH

When directed to check the pH of a solution, stir the solution thoroughly with a clean glass stirring rod and then touch the tip of the rod to a piece of litmus paper. Several such tests may be performed on each strip of paper. Never insert the test paper into the test tube since the chemicals on the paper could contaminate the contents. Red litmus paper will turn blue in basic solutions; blue litmus paper will turn red in acidic solutions.

General Safety Tips

Add all reagents gradually. Heat may be evolved, and the solution could become hot enough to boil. This is most likely to occur when neutralizing strong acids and bases. If a gas is evolved, such as when dissolving a carbonate solid in acid, the solution could bubble out of the test tube. Never hold a test tube so the open end is pointing at anyone. Never smell the contents of a test tube directly. If directed to check an odor, hold the test tube about 15 cm from your face, and gently waft any fumes from the top of the test tube toward your nose.

How to Describe Mixtures

Always describe the color and clarity of mixtures and reagents before mixing and what the mixture looks like after mixing, heating, centrifuging, etc. For example the following might be recorded for the first steps of this experiment.

- Starting unknown solution-clear and colorless
- 6 M HCl-clear and colorless
- Add 8 drops of the HCl to the unknown solution and stir mixture. A cloudy white, precipitate formed.
- After centrifuging, white precipitate settles to bottom, clear and colorless supernatant.

Common Reagents

Some common reagents and their uses in qualitative analysis are listed Table 1. You should become familiar with these reagents and their uses.

Table 1: Common Reagents in Qualitative Analysis

Reagent	Effect on System and Uses
6 M HCl	Raises $[H^+]$; lowers $[OH^-]$; dissolves insoluble hydroxides, carbonates, chromates and some sulfides; destroys hydroxo and NH_3 complex ions; increases $[Cl^-]$ causing precipitation of insoluble chlorides.
6 M NaOH	Raises $[OH^-]$; lowers $[H^+]$; precipitates insoluble hydroxides; forms hydroxo-complex ions.
6 M NH_3	Raises $[OH^-]$; lowers $[H^+]$; forms NH_3 complex ions; precipitates insoluble hydroxides; forms a basic buffer solution with NH_4^+ .
6 M HNO_3	Raises $[H^+]$; lowers $[OH^-]$; dissolves insoluble hydroxides, carbonates and chromates; destroys hydroxo and NH_3 complex ions; a good oxidizing agent when hot; dissolves insoluble sulfides by oxidation of sulfide ion.

Procedure

Safety: Wear your safety glasses while performing this experiment. Lead and mercury salts are toxic, and chromates are known to be carcinogenic. Silver ion is corrosive and leaves a black stain on the skin. HCl, NH₃ and HNO₃ are irritants. Avoid contact and wash immediately if any is spilled or splashed on you.

Make certain to wash your hands thoroughly when you leave the laboratory.

Waste: As you perform the experiment, collect all waste solutions in a waste beaker. This mixture should then be discarded in the appropriate waste container. DO NOT POUR ANY OF THE SOLUTIONS DOWN THE DRAIN.

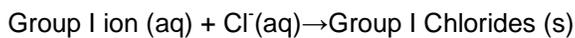
Note: The known is a mixture of equal volumes of 0.1 M AgNO₃, 0.2 M Pb(NO₃)₂ and 0.1 M Hg₂(NO₃)₂. Testing known samples is helpful in this analysis since doing so will allow you to observe what a positive test looks like. It is usually convenient to test a known sample simultaneously with your unknown.

Your unknown may contain Ag⁺, Hg₂²⁺ and/or Pb²⁺ ions.

Record your unknown number in your notebook.

Precipitation of Group I Chlorides

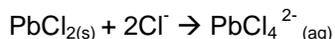
1. Add 8 drops of 6.0 M HCl to 2.0 mL of the sample. Shake the sample gently for two minutes to mix the sample. A white precipitate will form since Group I ions are present.



Centrifuge the solution, being careful to balance the centrifuge by placing test tubes containing equal volumes on opposite sides of the centrifuge.

After centrifuging your sample, add one more drop of the 6 M HCl to the solution to test for completeness of precipitation. If the solution turns cloudy (indicating that the precipitation is not complete), add 2 more drops of 6.0 M HCl, stir, centrifuge, and again test for completeness of precipitation. The supernatant must be free of Group I ions before moving on to the next step.

Be careful not to add too much HCl since it is possible to form chloro-complexes which are soluble. PbCl₂, in particular, tends to do this.



2. Decant the supernatant solution from the chloride precipitate. The solution can be discarded into a waste container since all of the ions we are interested in this experiment should be in the precipitate.

Separation and Identification of Pb²⁺

3. Half-fill a 100 mL beaker with distilled water and heat to near boiling.

4. Using a glass pipette and using caution with the hot distilled water, add 2.0 mL of the hot water to the test tube containing the precipitate.

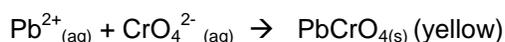
5. Place the test tube with the hot water and precipitate into the beaker of near boiling water. Heat for two minutes while gently stirring the sample with a glass rod to dissolve the lead (II) chloride.



Centrifuge the warm sample and decant the supernatant into a new, small test tube. This solution will be used in step 7.

6. To be sure all of the lead ions have been removed from the precipitate, repeat steps 4 and 5 above by adding 2.0 mL of hot distilled water to the precipitate, heating for two minutes in hot water, and centrifuging. Decant the supernatant into the same test tube containing the solution from the first washing (to be used in step 7). Save the precipitate for step 8.

7. To the solution from step 6, add 5 drops of 1.0 M K_2CrO_4 . A yellow precipitate of PbCrO_4 confirms the presence of lead.



Separation of Silver from Mercury, and Identification of Mercury (I) Ion

8. To the precipitate from step 6, add 10 drops of 4.0 M aqueous ammonia (aka ammonium hydroxide, NH_4OH). A black or gray residue confirms the presence of mercury(I).



In addition, the ammonia dissolves AgCl by forming the diammine silver complex ion.

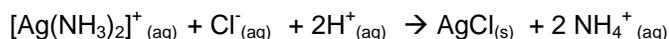


9. Centrifuge the sample and decant the solution into a new small test tube. Save the solution for step 11.

10. To be sure all of the silver has been removed from the precipitate, repeat steps 8 and 9 by adding an additional 10 drops of 4.0 M aqueous ammonia to the precipitate. Centrifuge the solution and again decant the supernatant into the same small test tube used in step 9. Save the solution for step 11.

Identification of Silver Ion

11. To the solution from step 10, add 6 M HNO_3 until it is acidic toward litmus paper. Test for acidity by dipping the end of your stirring rod in the solution and then touching it to a piece of blue litmus paper (blue litmus turns red in acid solution). If Ag^{+} is present in the acidified solution, a white precipitate of AgCl will form. The H^{+} from the nitric acid takes the ammonia away from the silver, freeing the silver ion to recombine with chloride.



12. Dispose of all waste in the proper containers.

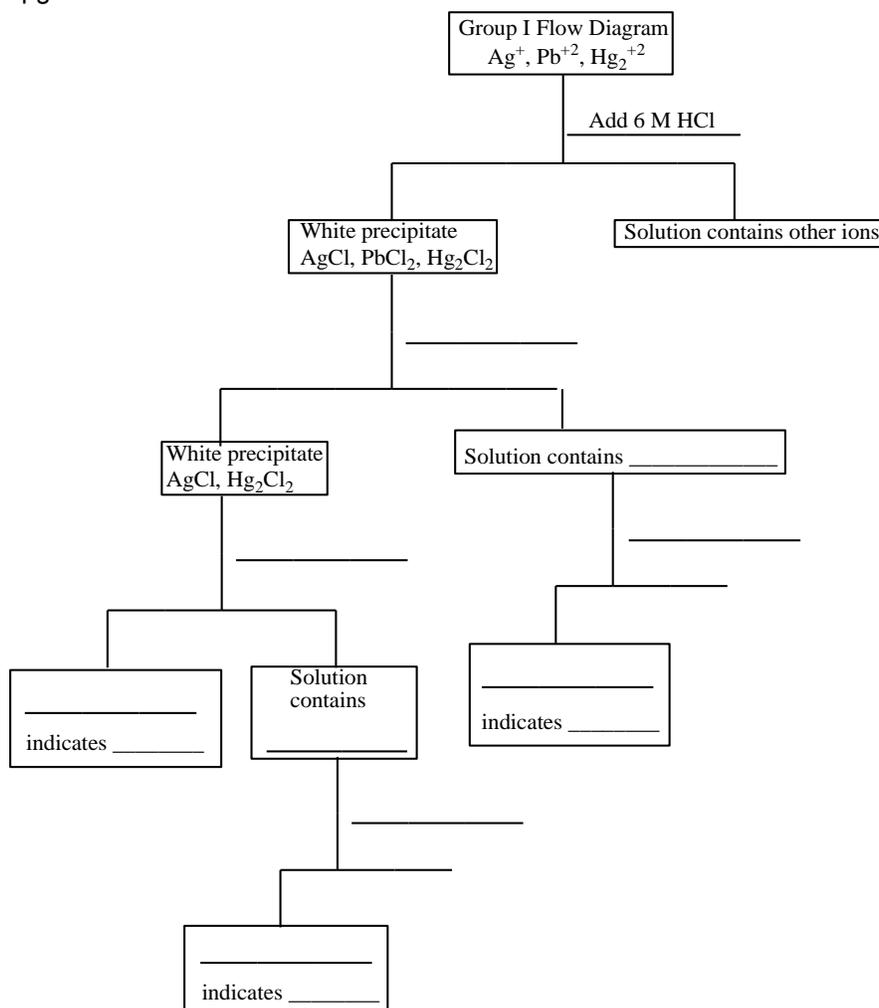
Data Tables

It is possible to summarize the directions for analysis of the Group I cations in what is called a flow diagram. In the diagram, vertical lines link successive steps in the procedure. Reactants are at the top end of each vertical line and products formed are at the bottom end. On the product end, a horizontal line separates the solid products on the left and the solution products on the right. Reagents and conditions used to carry out each step are placed alongside the lines. The chart has been filled in for step 1 of the procedure as an example.

Before coming to lab, study the procedure and then copy into your notebook the flow diagram shown below in the Procedure section of your lab notebook. Complete the flow diagram for the entire lab. Every line and box should be filled in.

In addition, under the diagram (or on the following page in your notebook), write the correct balanced reactions for each step of the lab for the known solution. Label them with the corresponding step in the lab and include phases for each substance (s, aq etc).

Finally, in your notebook organize two spaces where you will record your observations for the experiment- one space for the known and one for the unknown. An example of what you might record is on pg 4 of this lab under "How to Describe a Mixture".



Post-Lab Questions

For numerical problems, you must show all work for credit!

- Using the K_{sp} values given in the table on the first page of the lab, calculate the molar solubility of
 - AgCl
 - PbCl₂
- A 0.50 gram sample of AgCl(s) is shaken with 5.0 mL of 6.0 M NH₃ until there is no more net reaction. (K_f for Ag(NH₃)₂⁺ = 1.7×10^7)
 - Write the net ionic equation, including phase symbols, for the chemical reaction that occurs.
 - Does any solid AgCl remain? If so, what mass remains? (Hint: this is a solubility-complex ion question, NOT a limiting reactant problem!)
- Suppose 6 M NH₃ is accidentally added instead of hot water in the step 4. Is it still possible to identify the ions present using this sample? If identification is still possible, use a flow diagram to show the steps needed to complete the analysis.

Pre-Lab Questions

1. Explain why adding a slight excess of hydrochloric acid insures more complete precipitation of the Group I cations, but a large excess should not be used. Include the specific reaction we are trying to avoid involving Pb^{2+} .
2. What precautions need to be taken when
 - a. heating a solution?
 - b. centrifuging a solution?
3. Copy the flow chart on page 8-7 in your notebook. Complete all blank lines with the reagents you will be adding and each box with the products of the reaction.
4. For an unknown solution that contains at least one of the Group I cations, answer the following questions.
 - (a) Upon adding 6 M HCl to the unknown solution, a white precipitate forms. What cation(s) **may be present** in the unknown?

 - (b) When the white precipitate from (a) is treated with hot water, the white precipitate remains and a colorless supernatant is observed. The supernatant is pour into a new test tube. Adding $\text{K}_2\text{Cr}_2\text{O}_4(\text{aq})$ to the colorless supernatant results in no reaction. What conclusion can be made about the presence or absence of Group I cations in the unknown?

 - (c) When the precipitate from (b) is treated with 6 M $\text{NH}_3(\text{aq})$, it dissolves. If HNO_3 were then added to the resulting solution, what would you expect to observe? Give the balanced net ionic equation, including phase symbols, for the reaction that occurs upon addition of the HNO_3 .
5. A solution may contain Ag^+ , Pb^{2+} , and/or Hg_2^{2+} . A white precipitate forms when 6 M HCl is added. The precipitate is partially soluble in hot water. The supernatant and the precipitate are places into two separate test tubes. The solid remaining after treatment with hot water turns black on addition of 6 M NH_3 . The supernatant is tested with K_2CrO_4 and a yellow precipitate forms. No other precipitates are observed while preforming the procedure. Which of the ions are present and which are absent? State your reasoning.

NOTE: simply listing ions below without the appropriate reasoning will NOT earn you any credit!

6. Copy the flow chart you completed above in problem 3. However, now add the balanced chemical equations for each step. Keep in mind that your reactants should match the compounds that you start with in the flow chart and the products should match the compounds that start the next step.