EXPERIMENT 5
Qualitative Analysis of Group I Cations

SEMI-MICRO ANALYSIS

Qualitative analysis is the branch of analytical chemistry concerned with the identifying the constituents within a sample of material by systematic methods. In the case of inorganic substances, the sample is dissolved in an aqueous solution and its components are analyzed as cations or anions.

The qualitative experiments you will perform feature semi-micro methods of analysis which are adaptations of macroscopic methods to relatively small quantities of material – masses on the order of 10 to 50 mg for solids and volumes anywhere from 1 drop to 2 mL for liquids. Although semi-micro methods are no more sensitive than their macroscopic counterparts; they are more rapid and require less in the way of chemicals and apparatus. Some of the techniques to be used will now be enumerated.

1. MEASUREMENT AND TRANSFER OF LIQUIDS. Samples and reagent solutions are conveniently found in dropper bottles. Since each drop delivered by an ordinary dropper has a volume of approximately 0.05 mL (20 drops per mL) counting drops as they are transferred affords a way of measuring a quantity of liquid.

2. MIXING. Sample and reagent solutions are generally mixed in test tubes using vortex mixers. Holding the test tube firmly at the top, press the bottom of the test tube onto the rubber cup of the vortex mixer to agitate the contents. To mix a solution manually, and if a tube is not more than half filled, flick the bottom of the tube with a finger while holding it firmly at the top. If the tube is close to being filled, it is wise to pour the contents back and forth from one tube to another. Mixing may also be done with a glass stirring rod, although this is rather inefficient; there is always the chance of pushing the rod through the bottom of the tube. Shaking the contents of a tube using a finger or cork as a stopper is likely to result in contamination.

3. TESTING pH. When testing the pH of a solution, use a stirring rod to transfer a drop of liquid to a piece of indicator paper. Never dip the paper directly into the solution.

4. PRECIPITATION. Precipitations are usually carried out in small test tubes suitable for centrifugation. Reagent solution is added drop by drop, with frequent mixing. Complete precipitation is often essential and may be tested for by adding another drop of reagent to the supernatant liquid above the settled precipitate following centrifugation. If no additional solid appears, precipitation is assumed to be complete; otherwise add more reagent, centrifuge, and repeat the test. In order to detect precipitate formation, the solutions involved should be clear; if necessary, centrifuge to settle suspended particles. A clear solution means transparent but not necessarily colorless.

5. HEATING. Many procedures are carried out at elevated temperatures to increase a reaction rate or coagulate a colloidal precipitate. Since heating the contents of a test tube directly over a burner flame may cause them to “bump”, this operation is properly carried out in a water bath. A simple water bath is a 250-mL beaker half filled with water, heated with a hot plate. The test tube can be set in the bath or suspended in the bath using a clamp.

6. EVAPORATION. Frequently, the volume of a liquid must be reduced by evaporation. If proper care is exercised to avoid spattering or overheating, liquid may be evaporated from a porcelain dish placed over a low burner flame. When a procedure calls for evaporation to dryness, withdraw the flame while a few drops of liquid remain; residual heat from the dish should complete the operation.
7. **CENTRIFUGATION.** In semi-micro analysis, the separation of a precipitate from a solution involves centrifugation rather than filtration. The tube containing the solid-liquid mixture is placed in a holder attached to the rotating head of a centrifuge, and a similar tube containing an equal volume of tap water placed in the opposite holder serves as a counterweight to prevent vibration. The revolution of the centrifuge head forces solid to the bottom of the tube where it usually becomes tightly packed in less than a minute. Unless there is a braking device, the rotation should be allowed to stop without interference.

8. **SEPARATION OF SUPERNATANT LIQUID FROM A PRECIPITATE.** Once a centrifugation is complete, clear supernatant liquid may simply be decanted into another tube or drawn off with a capillary pipet, while making sure not to disturb the solid.

9. **WASHING THE PRECIPITATE.** After the removal of supernatant liquid, the small amount of solution that remains along with a precipitate may serve as a source of contamination in later operations. In addition, foreign ions are likely to be absorbed by a precipitate as it forms. To remove these contaminants, the precipitate is washed. Although the wash liquid is often deionized water, occasionally a very dilute solution of the original precipitating agent is used. The liquid is added directly to the tube containing the precipitate and the mixture is thoroughly stirred. After centrifugation, the wash may be combined with the supernatant liquid previously removed; otherwise this liquid is discarded.

10. **GENERAL INSTRUCTIONS.** All equipment should be arranged in some orderly fashion on a laboratory desk top. Capillary pipets should be stored with their tips pointing downward so that liquid cannot get into their rubber bulbs. Test tubes should be kept in a rack. Clean and rinse (with deionized water) dirty glassware whenever the opportunity arises. To clean a capillary pipet, remove the rubber bulb and flush out the stem with a stream of deionized water. If this doesn’t work, soak the stem in a beaker of acid. Deteriorating bulbs should be replaced immediately. Cleanliness is essential in qualitative analysis since a small trace of contaminant can easily lead to erroneous conclusions. As always, laboratory records should be kept up to date. Each experimental operation should be thought out and reported in the laboratory report form before proceeding to the next step; noting color of solutions or precipitates is particularly important. The descriptions should be accompanied by appropriate chemical equations.

**PRINCIPLES OF QUALITATIVE ANALYSIS FOR CATIONS**

Very few cations can be easily identified in the presence of several others. As a result, an analysis usually begins with a systematic separation of cations into groups, a procedure, which relies on the consecutive addition of reagents that form precipitates with certain cations while leaving the others in solution. There are five cation groups in all and they are precipitated in the following order:

I. Hydrochloric acid group: chlorides insoluble in acidic media
II. Acidic hydrogen sulfide group: sulfides insoluble in 0.3 M hydrochloric acid
III. Basic hydrogen sulfide group: sulfides insoluble in buffered ammonia solution
IV. Carbonate group: insoluble carbonates
V. Soluble group: cations, which do not precipitate in the previous reactions

The first cations that can be precipitated out of an aqueous sample containing many cations are the insoluble chlorides: silver, mercury (I) and lead (II). By adding hydrochloric acid to the aqueous sample, these three cations are the only ones that will form precipitates with the chloride ion, and they are separated from all of the other cations. These three cations are therefore called the group I cations, and their precipitating agent is hydrochloric acid.
Following the separation of these group I cations from all of the others, the individual cations in the group can now be separated and identified, because all of these three cations may or may not be present. Each identification involves a specific reaction, that is, a reagent is introduced which reacts with the ion in question to form a precipitate or complex ion having a particular color.

**INTRODUCTION TO THE GROUP I CATIONS**

A systematic analysis of common cations in aqueous solution begins with the addition of hydrochloric acid to precipitate the insoluble chlorides of silver, mercury (I), and lead (II). Chloride salts of other cations are soluble, and hence these ions remain in solution.

\[
\begin{align*}
\text{Ag}^{+} (aq) + \text{Cl}^{-} (aq) & \rightarrow \text{AgCl} (s, \text{white}) \\
\text{Pb}^{2+} (aq) + 2\text{Cl}^{-} (aq) & \rightarrow \text{PbCl}_2 (s, \text{white}) \\
\text{Hg}_2^{2+} (aq) + 2\text{Cl}^{-} (aq) & \rightarrow \text{Hg}_2\text{Cl}_2 (s, \text{white})
\end{align*}
\]

Lead (II) ions sometimes do not precipitate out as the chloride salt if the water is warm because lead (II) chloride is soluble in hot water. To insure precipitation of lead (II) chloride, the water should be cold.

1. **LEAD (II) ION.** Since lead (II) is three times more soluble in hot water than in cold water, it is separated from silver chloride and mercury (I) chloride by placing the precipitates in hot water. The lead (II) chloride will dissolve and the supernatant liquid can be tested for lead (II) ions by adding a solution containing chromate ions. A yellow precipitate, lead (II) chromate, confirms the presence of lead (II) ions.

\[
\text{Pb}^{2+} (aq) + \text{CrO}_4^{2-} (aq) \rightarrow \text{PbCrO}_4 (s, \text{yellow})
\]

2. **MERCURY (I) ION.** The addition of aqueous ammonia to the remaining precipitates separates silver chloride from mercury (I) chloride. The silver ion forms a stable complex with ammonia, diamminesilver, which is soluble in water. This causes the silver chloride to dissolve.

\[
\text{AgCl} (s) + 2\text{NH}_3 (aq) \rightarrow \text{Ag(NH}_3)_2^+ (aq) + \text{Cl}^- (aq)
\]

In the ammonical solution, mercury (I) chloride undergoes a disproportionation reaction (one in which part of the mercury (I) is oxidized to mercury (II) and part is reduced to elemental mercury) to form a black precipitate. The color is due to finely divided metallic mercury.

\[
\text{Hg}_2\text{Cl}_2 (s) + 2\text{NH}_3 (aq) \rightarrow \text{Hg} (s, \text{black}) + \text{HgNH}_2\text{Cl} (s, \text{white}) + \text{NH}_4^+ (aq) + \text{Cl}^- (aq)
\]

Mercury (II) amidochloride is a white precipitate, but the black color of the mercury metal generally masks it or makes the precipitate appear gray.

3. **SILVER ION.** Acidification of the diamminesilver complex confirms the presence of the silver ion. The hydrogen ions tie up the ammonia as ammonium ions, thereby freeing the silver ion, which unites with chloride ion to form insoluble silver chloride.

\[
\text{Ag(NH}_3)_2^+ (aq) + 2\text{H}^+ (aq) + \text{Cl}^- (aq) \rightarrow \text{AgCl} (s, \text{white}) + 2 \text{NH}_4^+ (aq)
\]
PROCEDURE

0. Students will work individually for this experiment. Except for the laboratory handout, remove all books, purses, and such items from the laboratory bench top, and placed them in the storage area by the front door. For laboratory experiments you should be wearing closed-toe shoes. Tie back long hair, and do not wear long, dangling jewelry or clothes with loose and baggy sleeves. Open your lab locker. Put on your safety goggles, your lab coat, and gloves.

0. Your instructor will indicate how you will perform the qualitative analysis. You will either (1) use the first part of the lab period to conduct the analysis on the known sample and then the second part of the lab period to conduct the analysis on the unknown sample, or (2) use the full lab period to analyze the known sample and the unknown sample simultaneously. Make sure to paste the unknown code label on your flow chart in the space provided.

PART A – SEPARATION OF GROUP I CATIONS

0. All reagents for the qualitative analysis labs will be found on the Qual Wall, to the right of the white board. From the Qual Wall, observe individual solutions of Ag⁺, Hg²⁺, and Pb²⁺. To analyze the sample solution, take a centrifuge tube to the stock bottle of sample solution (containing Ag⁺, Hg²⁺, and Pb²⁺), found on the balance table. Dispense 2 mL of the sample solution into the centrifuge tube using the pipet pump, and label it with your name and as sample. Label all centrifuge tubes used in this and further qualitative analysis experiments. Observe the solution, and record your observations in the flow chart. For the second part of the lab period, or, if you are analyzing the known and unknown samples simultaneously, you will place 2 mL of the unknown solution into a clean centrifuge tube, and label it with your name and as unknown.

1. Obtain a bottle of 6 M hydrochloric acid from the Qual Wall. Add 10 drops of 6 M hydrochloric acid to the sample and centrifuge. Always balance the centrifuge before use by using a second centrifuge tube with an equal amount of liquid - the two centrifuge tubes should be placed directly across from each other in the centrifuge. Test for complete precipitation by adding 1 drop of the 6 M hydrochloric acid to the clear supernatant. If cloudiness is observed or a precipitate forms, add another drop, mix, and centrifuge. Repeat this process until no new precipitate forms upon addition of the 1 drop of 6 M hydrochloric acid.

   CAUTION: Wear gloves and use caution with the 6 M hydrochloric acid as it is a skin irritant. Do not let it contact your skin.

   Obtain two capillary pipets, one for your known and one for your unknown. Attach a latex bulb (found in your lab locker) to a capillary pipet, and use the capillary pipet to remove the clear supernatant from the solution. Discard the supernatant into a waste beaker on your lab bench. If you would have also been testing for the cations of Groups II through V today, you would have to save the supernatants because they contain the Group II through V cations.

   Wash any precipitate twice by adding 10 drops of cold, deionized water, then mix with the vortex mixer, centrifuge and decant. The washes can be discarded.

PART B – TEST FOR LEAD (II) IONS

2. Half fill a 250 mL beaker with deionized water and set it on a hot plate in your fume hood. Adjust the hot plate so that the water gently boils. Add 3 mL of the hot, deionized water to the precipitate from step 1, and mix the contents of the centrifuge tube with the vortex mixer to digest the precipitate. Place the centrifuge tube in the boiling water bath for 3 minutes. After 3 minutes, centrifuge quickly so the solution does not cool. While still warm, decant the supernatant into a separate, labeled centrifuge tube with a cleaned capillary pipet. Save the precipitate for step 4.
3. Allow the supernatant from step 2 to cool, and then add three drops of 6 M acetic acid and three drops of 1 M potassium chromate. A yellow precipitate (not a yellow solution) confirms the presence of the lead (II) ion. Centrifuging may be necessary for a positive test. After the lead (II) identification, discard the yellow precipitate and solution into the waste beaker on your lab bench.

PART C – TEST FOR MERCURY (I) IONS

4. If lead (II) ions were present, add 5 mL of hot water to the white precipitate from step 2, mix, heat it in the hot water bath for 3 minutes, centrifuge, decant, and discard the supernatant. Then, again add 5 mL of hot water to the white precipitate from step 2, heat it in the hot water bath for 3 minutes, centrifuge, and decant the supernatant into a clean centrifuge tube. Set aside the white precipitate. Test the supernatant for lead (II) ions by following the directions in step 3. If lead (II) ions are present (as indicated by the formation of a yellow precipitate), discard the yellow solid and solution, and repeat the addition of hot water to the white precipitate you set aside until no positive reaction to the lead test is obtained.

To the washed precipitate that is void of any lead (II) ions, add 2 mL of 6 M ammonia and mix. A black precipitate indicates mercury is present. The supernatant must now be isolated for step 5. Centrifuge and decant the clear supernatant with a capillary pipet into a separate centrifuge tube. To the precipitate add 1 mL more of 6 M ammonia, centrifuge, and combine the clear supernatant with the clear supernatant that was just separated. Save this supernatant for step 5. After the mercury (I) identification, discard the black precipitate into the waste beaker on your lab bench.

PART D – TEST FOR SILVER IONS

5. Acidify the supernatant from step 4 by adding 1 mL of 6 M nitric acid, mixing the solution with the vortex mixer, then testing to see if the solution is acidic with litmus paper. If the solution is not acidic, add 1 mL more of 6 M HNO₃, mix, and test again with the litmus paper. Continue this procedure until the solution is acidic, and then add 1 additional mL of 6 M HNO₃. A white precipitate confirms the presence of silver ions. Centrifugation may be necessary for a positive test. After the silver identification, place the white precipitate and solution into the waste beaker on your lab bench, and discard the contents of the waste beaker into the waste bottle in the fume hood.

6. Identify the cations present in your unknown and record them at the top of your Data Table.

7. All excess solutions (including any remaining unknown solution) should be disposed of in the Chem 1B Waste Container in the fume hood. Return the unknown test tube to the front counter.

8. Clean and wipe dry your laboratory work area and all apparatus. When you have completed your lab report have the instructor inspect your working area. Once your working area has been checked your lab report can then be turned in to the instructor.
The following is a flow chart for the separation and identification of the Group I cations.

$\text{Ag}^{+}$, $\text{Hg}^{2+}$, $\text{Pb}^{2+}$, and the cations of Groups II, III, IV, V

$[1] \ 6 \text{ M HCl}$

$\text{white solid (AgCl, HgCl}_2, \text{ PbCl}_2)$

$[(2) \text{ hot water}]$

$\text{solution (Groups II, III, IV, V)}$

$\text{save for Group II separation or discard}$

$\text{white solid (AgCl, HgCl}_2)$

$[(4) \ 6 \text{ M NH}_3]$

$\text{black, white solid (Hg, HgNH}_2\text{Cl)}$

$\text{Hg}^{2+}$

$[(5) \ 6 \text{ M HNO}_3]$

$\text{colorless solution (Ag(NH}_3)_2^+$

$\text{Ag}^+$

$\text{colorless solution}$

$\text{discard}$

$\text{colorless solution (Pb}^{2+})$

$[(3) \ 6 \text{ M HCl}_2\text{O}_3, \ 1 \text{ M K}_2\text{CrO}_4]$
**EXPERIMENT 5 LAB REPORT**

Name: ___________________________________________  Student Lab Score: ____________

Date/Lab Start Time: ___________________________  Lab Station Number: ________________

**KNOWN DATA TABLE**

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**UNKNOWN DATA TABLE**

**UNKNOWN _____**

**IONS PRESENT:**

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QUESTIONS

1. Why can the silver, mercury (I), and lead (II) ions be separated from all other cations in solution by the addition of hydrochloric acid? Indicate the reactions that occur.

_________________________________________________________________________

_________________________________________________________________________

_________________________________________________________________________

reaction: ___________________________________________________________________

reaction: ___________________________________________________________________

reaction: ___________________________________________________________________

2. Why can solid lead (II) chloride be separated from solid silver chloride and solid mercury (I) chloride by the addition of hot water?

_________________________________________________________________________

_________________________________________________________________________

_________________________________________________________________________

_________________________________________________________________________

3. Why can solid silver chloride be separated from solid mercury (I) chloride by the addition of aqueous ammonia? Indicate the reaction that occurs.

_________________________________________________________________________

_________________________________________________________________________

_________________________________________________________________________

_________________________________________________________________________

reaction: ___________________________________________________________________
4. In semi-micro qualitative analysis, why are precipitates washed?

5. What happens in step 1 if nitric acid is substituted for hydrochloric acid?

6. What happens in step 4 if sodium hydroxide is substituted for ammonia?

7. Identify each of the following:
   (a) a reagent that precipitates mercury (I) ions but not copper (II) ions
   (b) a reagent that dissolves lead (II) chloride but not silver chloride
   (c) a reagent that separates silver chloride from mercury (I) chloride