QUALITATIVE ANALYSIS OF GROUP I CATIONS

In previous labs you have determined the amount of an unknown species present, such as percent chloride, identification of an unknown copper, and the molarity of various acid and base solutions. These experiments are a part of chemistry called *quantitative analysis*. When a chemist performs a **qualitative** analysis of a sample, s/he is more interested in the nature of the species present in a sample rather than the amount.

A set of experiments can be performed on an unknown mixture to precipitate cations in a sequential order. Under specific conditions, if a precipitate contains only one cation, the presence of that cation can be determined. Various types of reactions can be performed to separate the ions, including acid-base, complex ion formation, redox and other precipitation reactions. Ultimately, the sample should be resolved into fractions each containing one cation, whose presence is established by the formation of a characteristic precipitate or colored complex ion. The first step is to develop a scheme for the separation and identification of the cations.

Over the next several weeks, you will study group I and III cations. You will develop a scheme to determine the cations present in an unknown mixture. Finally, you will carry out this scheme.

Precipitation and Separation of Group I Cations:

Pb^{+2}, Hg_2^{+2}, and **Ag^+** are all insoluble in cold water. They can be removed as a group from solution by the addition of HCl via simple precipitation:

$$Ag^+ + Cl^- \rightarrow AgCl_{(s)}$$

It is important to add enough HCl to ensure complete precipitation, but not too large an excess. In highly concentrated HCl solutions, chloro-complexes may form such as $AgCl_2^{-1}$.

Lead chloride can be separated from AgCl and Hg_2Cl_2 by heating with water, essentially reversing the above reaction. Once Pb^{+2} is in solution, you can discern its presence by adding chromate ion to produce a **yellow** solid:

$$Pb^{+2} + CrO_4^{-2} \rightarrow PbCrO_{4(s)} \text{ (yellow)}$$

Hg_2Cl_2 can be distinguished from AgCl by reaction with ammonia via oxidation reduction to yield finely divided black metallic mercury and a white complex compound $HgNH_2Cl$. As the reaction proceeds, the solid appears to change colors from white to **black** or **gray**:

$$Hg_2Cl_2\text{(white solid)} + 2\ NH_{3(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)} + Hg\text{(black liquid)} + HgNH_2Cl\text{(white solid)}$$

Silver chloride also reacts with aqueous ammonia to form a complex ion that remains in solution. Addition of a strong acid will destroy the complex and confirm the presence of silver ion by re-precipitating the **white** AgCl solid:

$$AgCl_{(s)} + 2\ NH_{3(aq)} \rightarrow Ag(NH_3)_2^+{}_{(aq)} + Cl^-{}_{(aq)}$$
$$Ag(NH_3)_2^+{}_{(aq)} + 2\ H^+{}_{(aq)} + Cl^-{}_{(aq)} \rightarrow AgCl_{(s)} + 2\ NH_4^+{}_{(aq)}$$

Flow Charts: It is possible to summarize the directions for analysis of the Group I cations in a flow chart. In the diagram, successive steps in the procedure are linked with arrows. Reactant cations are at one end of the arrow; reagents and conditions used to carry out each step are placed alongside the arrows. The arrow splits to show the two possible outcomes (yellow ppt = Pb^{+2} present; no ppt = absence). A **flow chart** for the separation of Group I cations should be included in your lab report.

PROCEDURE: *Be sure to include a **Flowchart** with your lab report. All waste must go in a waste bottle.*

Prepare a 1 mL "known" sample by placing 7 drops of each of the following into a centrifuge tube: 0.1 M $AgNO_3$, 0.3 M $Pb(NO_3)_2$ and 0.5 M $Hg_2(NO_3)_2$. Prepare a second 1 mL "unknown" sample using 1 mL of your unknown liquid. Be sure to write the identity of your unknown. Your unknown will have between one and three of the Group I cations in it, and the known will act as a "control" to see appropriate color changes, etc. throughout the tests.

You will perform the following tests upon *each* solution (both the known and unknown solutions) simultaneously. Be sure to write down any color changes, precipitates, etc. that you might observe.

Step 1: Precipitation of Group I Cations:

Add two drops of 6 M HCl and mix with a clean stirring rod. Centrifuge the mixture being certain a centrifuge tube of equal volume is placed opposite your centrifuge tube as a balance. Add one more drop of 6 M HCl to the test tube to be certain of complete precipitation. Centrifuge again if necessary. Decant the supernatant into another test tube and save for later analysis for Group III cations (if appropriate). The precipitate should be white and contain the chlorides of the Group I cations.

Step 2: Separation and ID of Lead:

Rinse the precipitate with 1-2 mL of deionized water. Stir, centrifuge and discard the liquid. Add 2 mL deionized water and place in boiling water for two minutes, stirring occasionally to dissolve most of the $PbCl_2$. Centrifuge and decant the liquid into another test tube. Save the precipitate for later tests for silver and mercury.

Add one drop of 6 M acetic acid and two drops of 1 M K_2CrO_4 to the liquid. A bright yellow precipitate will appear if the lead (II) ion is present.

Step 3: Separation and ID of Mercury:

To the precipitate from step 2, add 1 mL 6 M NH_3 and stir. Centrifuge and decant the liquid into a test tube. A gray or black precipitate confirms the presence of the mercury(I) ion.

Step 4: Identification of Silver:

Add 6 M HNO_3 to the liquid from step 3 until it is acidic to litmus. Test for acidity by touching the end of your stir rod to litmus paper. If Ag^+ is present, it will precipitate in the acidified solution as white AgCl.

POSTLAB QUESTIONS:

1. Write balanced net ionic equations for the following reactions:
   a. The precipitation reaction of the chloride of Hg_2^{+2} in step 1.
   b. The formation of the yellow precipitate in step 2.
   c. The formation of the black precipitate in step 3.
   d. The reaction that occurs in step 4.

2. A solution may contain one or more of the Group I cations. A white precipitate forms on addition of 6 M HCl. The precipitate appears partially soluble in hot water; the residue dissolves on addition of 6 M NH_3. Which of the ions are present? Which are absent? Which remain undetermined? Explain your reasoning. If any cations remain undetermined, what reaction could you perform to confirm or disprove its presence?