**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, Hg2**

**+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- →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 AgCl2

-1.

**Lead** chloride can be separated from AgCl and Hg2Cl2 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 + CrO4

-2 →PbCrO4(s) (yellow)

**Hg2Cl2** can be distinguished from AgCl by reaction with ammonia via oxidation reduction to yield finely divided

black metallic mercury and a white complex compound HgNH2Cl. As the reaction proceeds, the solid appears to

change colors from white to **black** or **gray**:

Hg2Cl2(white solid) + 2 NH3(aq) →NH4

+

(aq) + Cl-

(aq) + Hg(black liquid) + HgNH2Cl(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 NH3(aq) →Ag(NH3)2

+

(aq) + Cl-

(aq)

Ag(NH3)2

+

(aq) + 2 H+

(aq)

+ Cl-

(aq) →AgCl(s) + 2 NH4

+

(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.

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**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 AgNO3,

0.3 M Pb(NO3)2 and 0.1 M Hg2(NO3)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 PbCl2. 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 K2CrO4 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 NH3 and stir. Centrifuge and decant the liquid into a test tube for

testing for Ag+. A gray or black precipitate confirms the presence of the mercury(I) ion. Add two drops of K2CrO4

to confirm the yellow-brown Hg2CrO4.

**Step 4: Identification of Silver:**

Add 6 M HNO3 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. Add two drops of

chromate to confirm Ag+ by the appearance of solid red Ag2CrO4.

**POSTLAB QUESTIONS:**

1. Write balanced net ionic equations for the following reactions:

a. The precipitation reaction of the chloride of Hg2

+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 NH3. 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