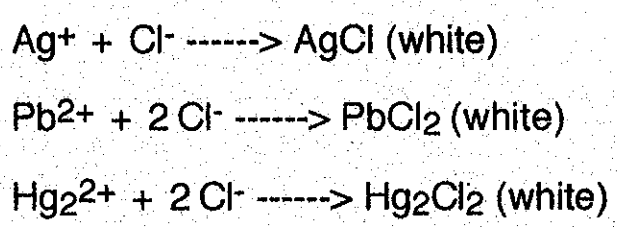
GROUP I ANALYSIS

(Ag^{+}, Hg_2^{2+}, Pb^{2+})

The Group I cations are silver, mercury and lead. They are put together as a group because they can be easily separated from other cations by forming chloride precipitates. These chlorides are formed by the addition of HCl to solution. Unfortunately all three chloride precipitates are white and therefore indistinguishable from each other. Further separation is required to determine which cations are present in an unknown. The process of separation and identification of Group I cations is given in the following pages. The initial discussion does not include concentration or amounts to be used. It is simply on overview of the reactions taking place. The exact procedure is listed under experimental procedure and follows the discussion. The separation procedure is also shown using a flow chart.

PRECIPITATION AND SEPARATION OF GROUP I IONS: (Reactions)

1. Group I cations are separated from solution by the addition of HCl. The ions form chlorides which are insoluble in cold water:

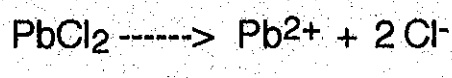


$Ag^{+} + Cl^{-} \text{------>} AgCl$ (white)

$Pb^{2+} + 2\,Cl^{-} \text{------>} PbCl_2$ (white)

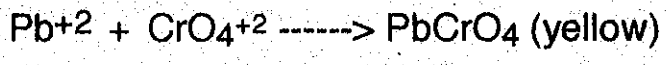
$Hg_2^{2+} + 2\,Cl^{-} \text{------>} Hg_2Cl_2$ (white)

2. Lead chloride is separated from the other two chlorides by heating with water. The lead chloride dissolves in hot water:



$PbCl_2 \text{------>} Pb^{2+} + 2\,Cl^{-}$

3. Once the lead ion is returned to solution, we can check for its presence by adding a solution of potassium chromate. The chromate gives a yellow precipitate with lead:



$Pb^{+2} + CrO_4^{+2} \text{------>} PbCrO_4$ (yellow)

4. The silver chloride and the mercury chloride can be separated by adding aqueous ammonia. Silver chloride dissolves, forming an ammonium complex:

$$AgCl + 2\,NH_3 \text{-----> } Ag(NH_3)^{2+} + Cl^-$$

5. The solution containing $Ag(NH_3)^{2+}$ needs to be further tested to establish the presence of silver. The addition of nitric acid to the solution destroys the complex ion and reprecipitates silver chloride. Consider the reaction in two steps:

$$Ag(NH_3)^{2+} + 2\,H^+ \text{----> } Ag^+ + 2\,NH_4^+$$

$$Ag^+ + Cl^- \text{------> } AgCl \text{ (white)}$$

6. Ammonia also reacts with mercury chloride. The product includes finely divided metallic mercury, which is black, and a compound of formula $HgNH_2Cl$, which is white:

$$Hg_2Cl_2 + 2\,NH_3 \text{----> } Hg + HgNH_2Cl + NH^{4+} + Cl^-$$

EXPERIMENTAL PROCEDURE: (Group I)

1. **Group Precipitation**
   A. Obtain 2-3 ml of group I solution or unknown.
   B. Add 2 drops of 6 M HCl and centrifuge.
   C. Add one more drop of HCl to the solution to make sure precipitation is complete. If more precipitate forms, centrifuge. Repeat the process until no more precipitate forms.
   D. Decant and save the precipitate for step #2. Discard the decantate. (NOTE: DO NOT discard when doing unknowns. Save for group III analysis.)
   E. (Do this step only if doing unknowns.) Wash the precipitate by adding 1 drop of 6 M HCl and 10 drops of water. Centrifuge and discard the decantate.

2. **Separation of lead**
   A. Add 1 ml (20 drops) of water to the precipitate from step #1.
   B. Heat the solution in a hot water bath for 3 minutes, stirring occasionally.

IMPORTANT: It is essential to thoroughly mix the hot mixture and to centrifuge and decant while the solution is still hot. Also, step #3 must be done immediately after step #2.

C. Centrifuge the hot solution and quickly pour the liquid into another test tube. Save the liquid for step #3 and the precipitate for step #4. The confirmation of lead test(step #3) must be done immediately. Do not allow this hot solution to cool.

3. **Confirmation of lead**
   A. To the hot decantate from step #2, add 2 drops of 0.5 M $K_2Cr_2O_7$. Centrifuge.
   B. The presence of lead is verified by the formation of a yellow precipitate, $PbCrO_4$.

4. **Separation and identification of mercury**
   A. Use the precipitate from step #2. (If this precipitate is yellow, repaeat the hot water treatment as follows: Add 20 drops of H_2O and heat in a hot water bath for 3 minutes, stirring frequently. Centrifuge and decant. Discard the decantate.) Once you obtain a white, gray, or black precipitate, you can continue.
   B. If the precipitate cannot be analyzed during the class period in which it was obtained, it must be stored in a <u>dark</u> place until the next class period.
   C. Add 5 drops of 15 M NH_3 to the precipitate. Centrifuge and decant. <u>Save the decantate for step #5</u>.
   D. A gray-black or white-gray precipitate establishes the presence of mercury. The presence of a pure white precipitate at this point does <u>not</u> confirm the presence of mercury.

5. **Confirmation of silver**
   A. Add 16 M HNO_3 to the decantate from step #4 until acidic (use litmus paper). **IMPORTANT**: The solution must be acidic. Add a few extra drops to make sure.
   B. If silver is present in the acidic solution, a white precipitate, AgCl, will form.

A flow chart summarizing the above directions is shown on the next page.It is usually easier and quicker to use the flow chart during the actual lab procedure.

Analysis Scheme for Group I Cations

Group I Flowchart