國立中正大學

National Chung Cheng University

The university motto of National Chung Cheng University

積極創新 修德澤人

Strive for Innovation, Cultivate Virtue to Benefit Others

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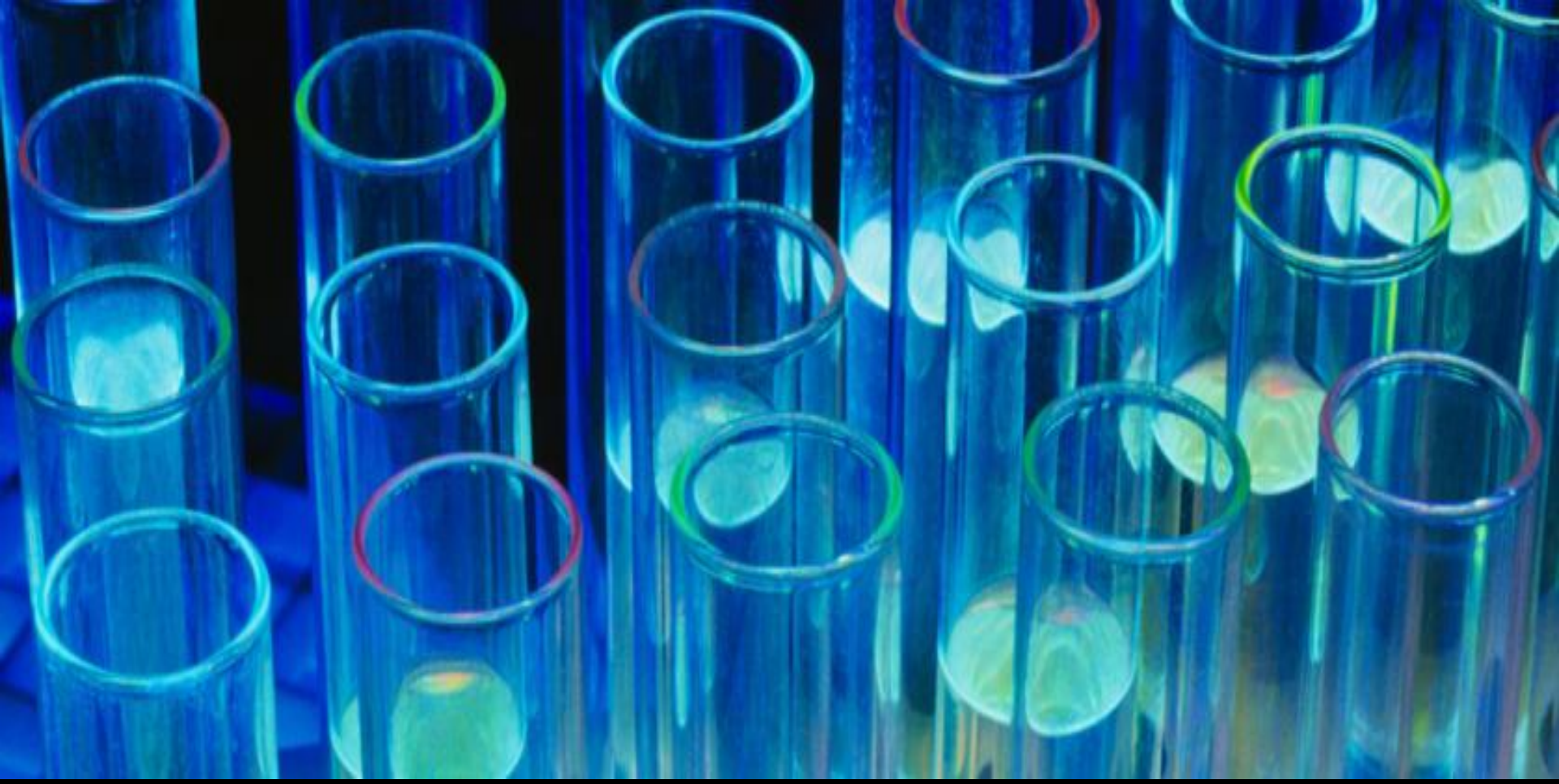


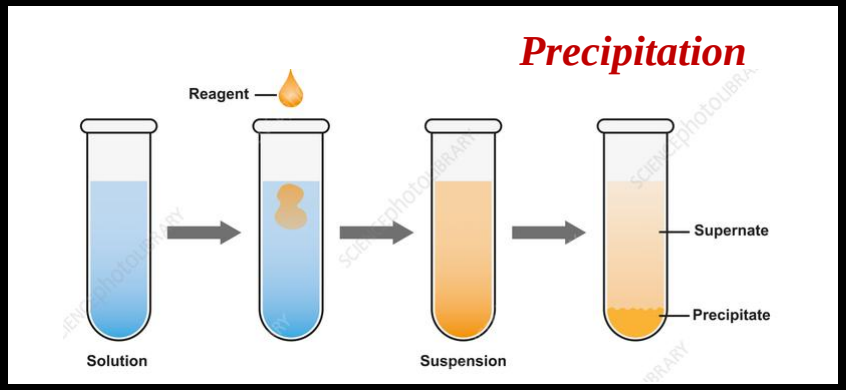
114-2 EMI General Chemistry Laboratory

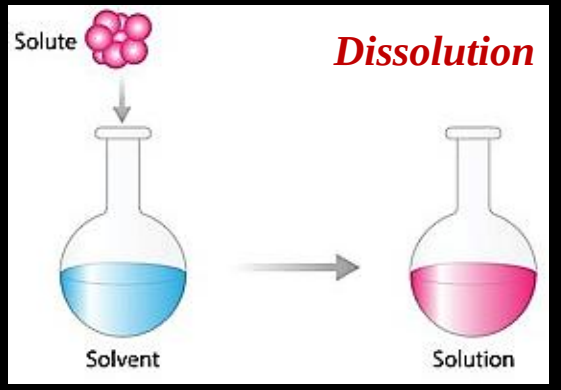
Expt. 5 - Group I Cation Qualitative Analysis

115.05.08 (time required: 2 hours)

1. Objective

- Master techniques for the separation and identification of common metallic cations.
- Understand equilibrium principles involving ***precipitation***, ***dissolution***, and ***complex ion formation***.
- Develop systematic logic for analytical chemistry procedures.





$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

$$Ag^{+}(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^{+}(aq)$$ ***Complex Ion Formation***

2. Principle

- **Stages of Qualitative Analysis**

1. Group Separation

Cations are separated into 5 groups based on solubility properties using sequential selective reagents.

2. Selective Dissolution

Within each group, precipitates are selectively dissolved and separated based on chemical behavior.

3. Identification

Presence of individual cations is confirmed through specific, characteristic identification tests.

Classification of Cations into Five Groups :
Based on the solubility of their salts

1. Group I: Ag^{+} , Hg_2^{2+} , and Pb^{2+} – form insoluble chlorides.
2. Group II: Hg^{2+} , Pb^{2+} , Cu^{2+} , Bi^{3+} , Cd^{2+} , As^{3+} , Sb^{3+} , and Sn^{4+} – form insoluble sulfides in acidic solution.
3. Group III: Al^{3+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cr^{3+} , Zn^{2+} , and Mn^{2+} – form insoluble sulfides or hydroxides in basic solution.
4. Group IV: Ca^{2+} , Sr^{2+} , Ba^{2+} , and Mg^{2+} – form insoluble carbonates.
5. Group V: Na^{+} , K^{+} , and NH_4^{+} – remain soluble in all common reagents.

Note: In this experiment, only Group I cation analysis will be performed.

Characteristics of Group I Cations

Group I consists of Ag^+, Hg_2^{2+}, and Pb^{2+}.

These are known as the Insoluble Chloride Group.

Standard Solubility Principle:

$$X^{n+}(aq) + nCl^-(aq) \rightarrow XCl_n(s)$$

Hazard Note: These cations and their chloride precipitates are toxic. Handle with extreme caution in the lab.

Properties of Group I Cations Ag^{+}, Hg_2^{2+}, Pb^{2+}

- Under acidic conditions, these cations form insoluble chlorides—AgCl(s), Hg_2Cl_2(s), and $PbCl_2$(s)—which allow them to be separated from cations of the subsequent groups.
- Due to differences in the solubility product constants (K_{sp}) and the ability to form complex ions, Group I cations can be individually identified.

* **This experiment involves chlorides that are hazardous to human health. Even short-term exposure may cause serious or potentially fatal harm. To ensure your safety, please strictly adhere to all laboratory safety regulations while conducting this experiment.**

3. Equipment and Chemicals

Equipment

In Cabinet	Provided by TA
Hot plate stirrer	Centrifuge tubes x 3
Beaker 100 mL x 1	Centrifuge
Test tubes x 5	Dropper
Glass stirring rod x 1	Blue litmus paper

Chemicals

Standard Cation Solution (10 mg of each cation / mL)

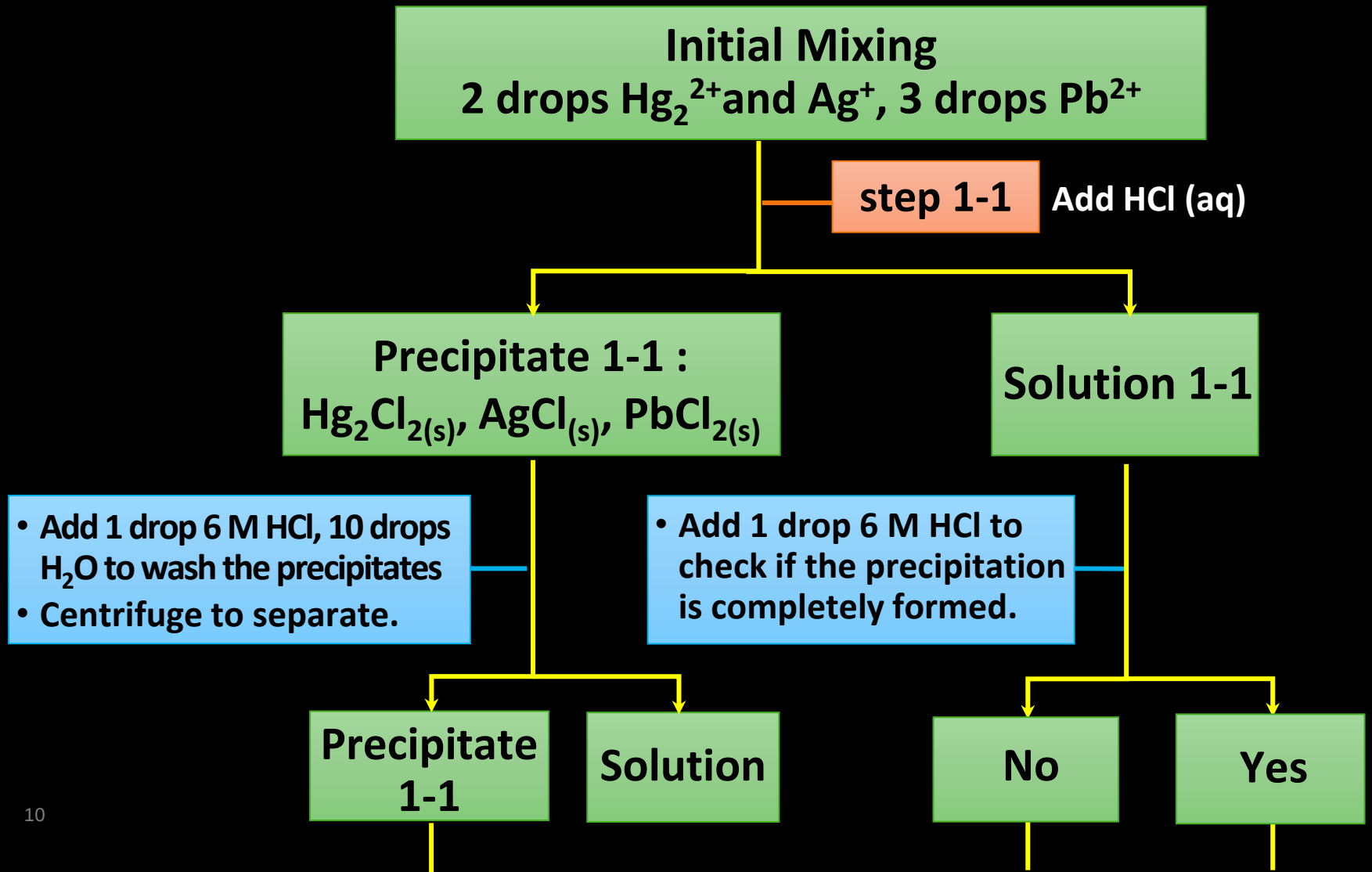
Hg_2^{2+}* ：	$Hg_2(NO_3)_2 \cdot 2H_2O$
Ag^{+}** ：	$AgNO_3$
Pb^{2+}** ：	$Pb(NO_3)_2$

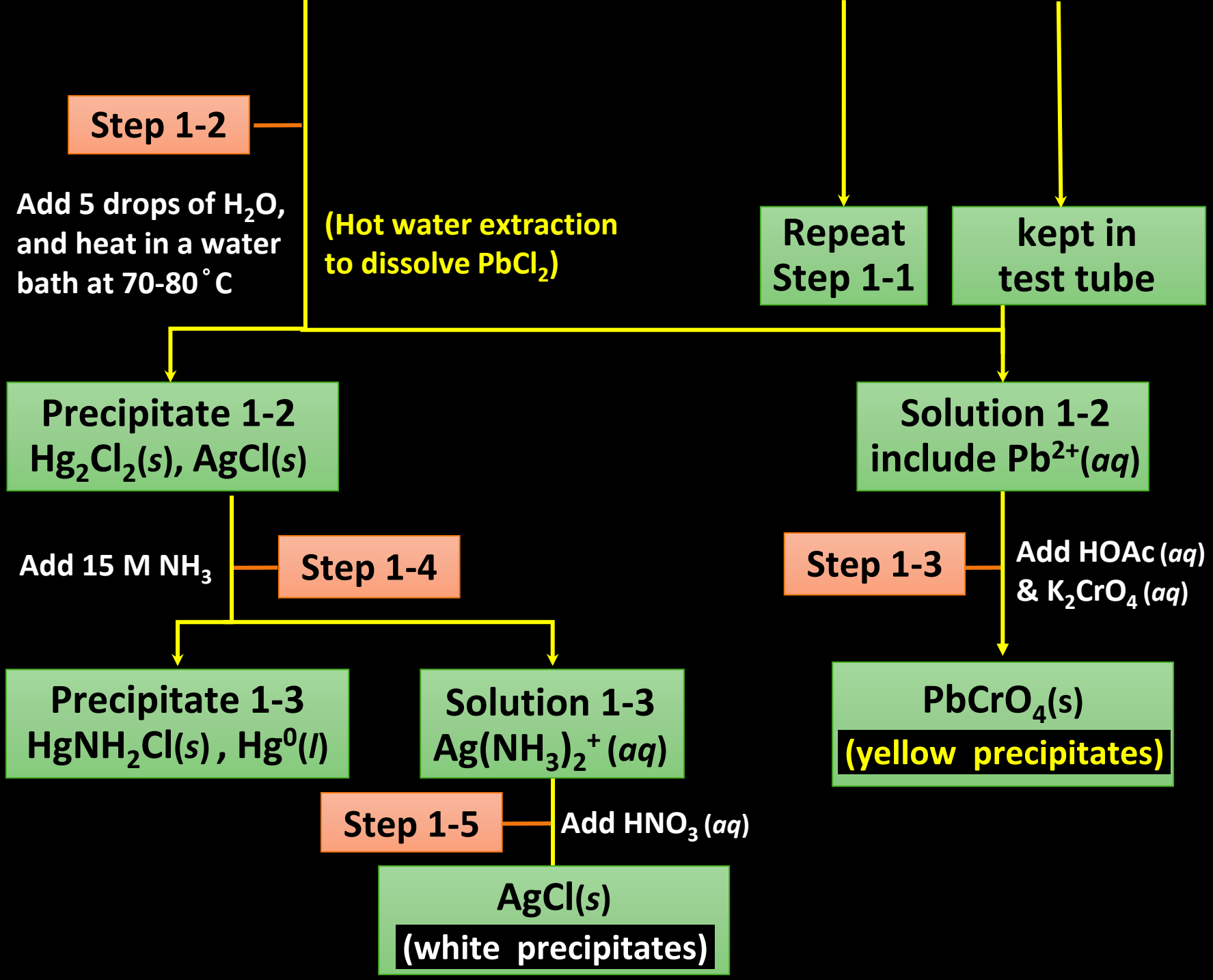
Reagents

6.0 M HCl ***	0.5 M K_2CrO_4**
6.0 M CH_3COOH****	6.0 M HNO_3)****
15.0 M NH_3**	Reference materials：https://pubchem.ncbi.nlm.nih.gov/

* ： Toxic
* ： Dehydrating
* ： Flammable
* ： Corrosive

4. Systematic Separation Flowchart




Step 1-2
Add 5 drops of H_2O, and heat in a water bath at 70-80˚C
(Hot water extraction to dissolve $PbCl_2$)
Repeat Step 1-1
kept in test tube
Precipitate 1-2
$Hg_2Cl_2(s)$, $AgCl(s)$
Solution 1-2
include $Pb^{2+}(aq)$
Add 15 M NH_3
Step 1-4
Step 1-3
Add HOAc (aq) & K_2CrO_4 (aq)
Precipitate 1-3
$HgNH_2Cl(s)$, $Hg^0(l)$
Solution 1-3
$Ag(NH_3)_2^+$ (aq)
$PbCrO_4(s)$
(yellow precipitates)
Step 1-5
Add HNO_3 (aq)
$AgCl(s)$
(white precipitates)

5. Experimental Procedures

Step 1-1 : Chlorides

1. Add one drop of 6 M HCl (aq) to the centrifuge tube and shake gently for 1–2 minutes. If a precipitate forms, allow it to settle at the bottom. Then, add another drop of 6 M HCl (aq) to check if precipitation is complete. Continue adding HCl dropwise until no further precipitate forms.

   Note 1 : $PbCl_2$ precipitates slowly; shaking helps ensure complete precipitation.

   Note 2 : HCl must be added dropwise to prevent excessive addition, which may lead to chloride dissolution.

2. After centrifugation, carefully decant the clear supernatant into a separate test tube. Label this as ***Solution 1-1***.

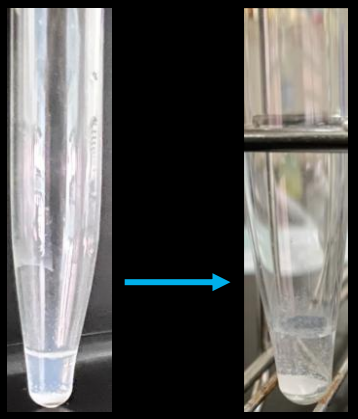


Figure 5.1 – *$PbCl_2$ settling at the bottom of the centrifuge tube after standing undisturbed.*

$$X^{n+}_{(aq)} + nCl^-_{(aq)} \rightleftharpoons XCl_n(aq)$$

($X = Hg^{2+}$; Ag^+)

Step 1-2 : Lead Confirmation-I (Temperature Separation)

3. Add 5 drops of deionized water to the precipitate from ***Solution 1-1***. Heat and stir the mixture in a water bath at 70–80°C for several minutes.

4. Quickly centrifuge the mixture, then transfer the clear supernatant to a new test tube. Label this as ***Solution 1-2***.

   Note: If the solution is allowed to cool for too long, $PbCl_2$ may re-precipitate.

$$PbCl_{2(s)} \overset{\Delta}{\rightleftharpoons} Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$

Step 1-3 : Lead Confirmation-II ($PbCrO_4$ Precipitate Formation)

5. To ***Solution 1-2***, add 1 drop of 6 M CH_3COOH (aq) followed by 4 drops of K_2CrO_4 (aq). The formation of a yellow precipitate indicates the presence of Pb^{2+}.
   Note: CH_3COOH (aq) is added to prevent the precipitation of chromates that are not associated with Pb^{2+}.

6. If Pb^{2+} is confirmed in ***Solution 1-2***, continue extracting the precipitate from ***Precipitate 1-1*** using hot deionized water until the extracted solution becomes slightly cloudy upon the addition of K_2CrO_4 (aq).

$$Pb^{2+}_{(aq)} + K_2CrO_{4(aq)} \rightleftharpoons PbCrO_{4(s)} + 2K^+_{(aq)}$$

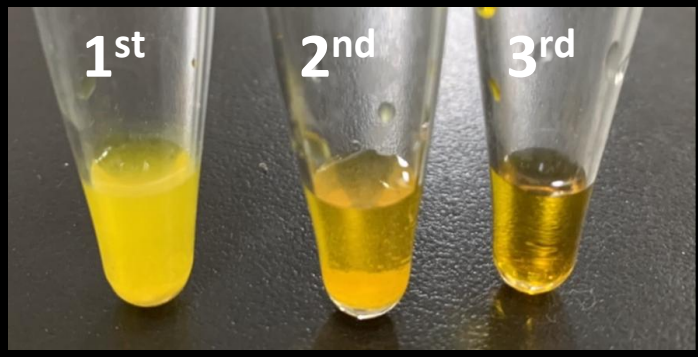


Figure 5.2 – After the 3rd extraction, the solution appears significantly clearer.

Step 1-4 : Mercury Disproportionation

7. Add 4 drops of 15 M concentrated ammonia to the *Precipitate 1-2* that no longer contains Pb^{2+}. Gently shake the centrifuge tube to fully disperse the precipitate.

   Note: Incomplete removal of Pb^{2+} may interfere with subsequent test results.

8. After centrifugation, transfer the supernatant to a new test tube (***Solution 1-3***), and observe the color of the remaining precipitate (***Precipitate 1-3***).

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^{2+}(aq) + Cl^-(aq)$$

$$Hg_2Cl_2(s) + 2NH_3(aq) \rightleftharpoons Hg(l) + HgNH_2Cl(s) + NH_4^+(aq) + Cl^-(aq)$$

Figure 5.3 – The formation of a black precipitate, a mixture of $HgNH_2Cl(s)$ and $Hg(l)$, indicates the presence of Hg_2^{2+} ions.

Step 1-5 : Silver Re-precipitation (Acidification Confirmation)

9. Add 6 M HNO_3 (aq) to ***Solution 1-3*** to acidify the solution, and observe any changes. The formation of a white precipitate indicates the presence of Ag^+ ions.

Note: After adding the acid, mix the solution thoroughly and confirm its acidity using pH paper.

$$Ag(NH_3)^{2+}_{(aq)} + Cl^-_{(aq)} + 2H^+_{(aq)} \rightleftharpoons 2NH_4^+{}_{(aq)} + AgCl_{(s)}$$

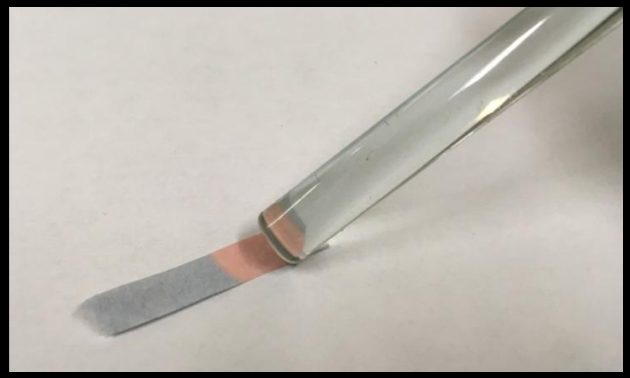


Figure 5.4 – The blue litmus paper turned red, confirming that the solution is acidic.

Step 1-6 : Final Clean Up

10. Please retain all separated and identified precipitates, along with your recorded experimental results, for the TA's review.
11. Collect all waste solutions containing heavy metals and dispose of them in the designated heavy metal waste container.
12. Thoroughly clean all glassware used during the experiment, and remove any labels from centrifuge tubes by scrubbing them off.

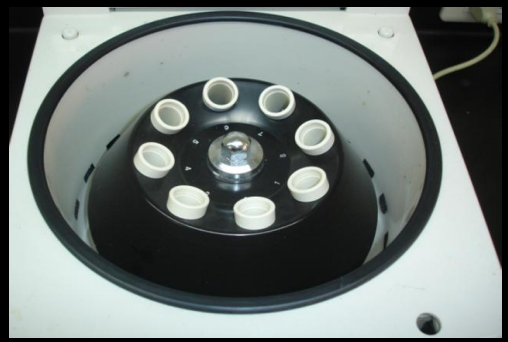
6. Safety Precautions

1. **Fume Hood Requirement:** This experiment involves corrosive vapors (HCl, NH_3). All heating and reagent handling ***must*** be processed in the fume hood.
2. **Heavy Metal Toxicity**: Ag^+, Hg_2^{2+}, and Pb^{2+} ions are ***highly toxic***. Handle with extreme care and avoid contamination.
3. **Mandatory PPE:** Full protective gear (lab coat, goggles, gloves, and mask) is required at all times.
4. **Safety Compliance:** Strictly follow all laboratory regulations and TA instructions regarding hazardous chemicals.
5. **No Removal Policy:** Taking any chemicals or equipment out of the laboratory is strictly prohibited for safety and security reasons.

The Front Panel of The Centrifuge

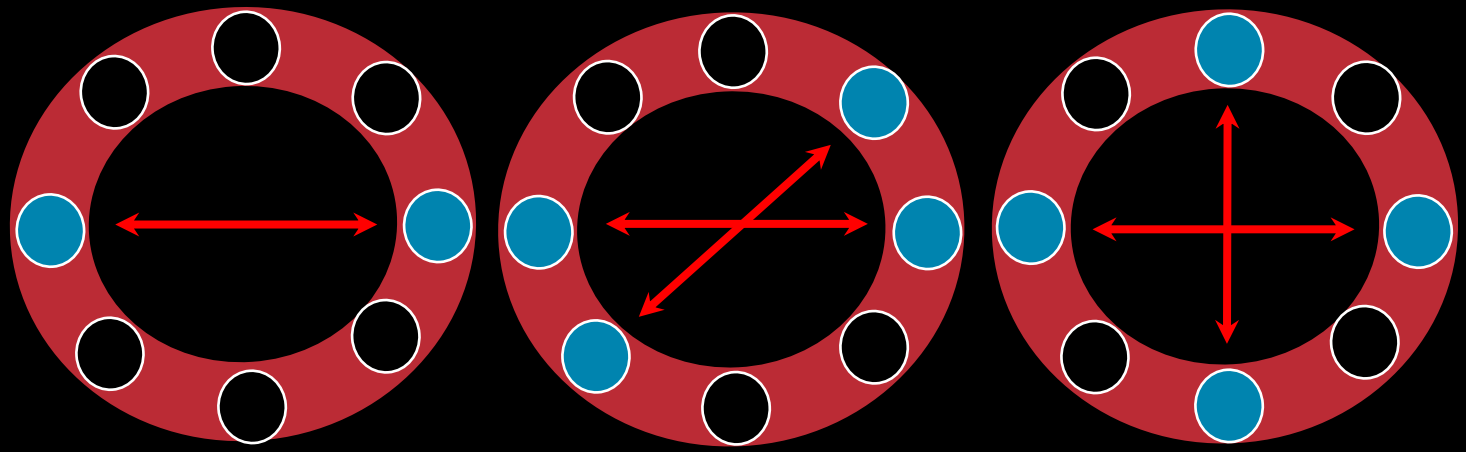
Instruction for Using The Centrifuge-1

1. Turn on the power and ensure the centrifuge is completely stationary. Then, press the release button to open the lid. **Caution: The lid cannot be opened unless the power is turned on.**
2. Before use, inspect each centrifuge tube to ensure it is intact. If there is any sign of corrosion, damage, or the presence of unknown substances, the tube must be thoroughly cleaned or replaced before operation.



Instruction for Using The Centrifuge-2

3. Ensure that centrifuge tubes are balanced by placing them in pairs directly opposite each other. If there is an odd number of tubes, use an additional tube filled with water as a counterbalance to maintain symmetry and prevent damage during centrifugation.



Instruction for Using The Centrifuge-3

4. When closing the centrifuge lid, ensure it is securely locked in place before turning on the power.
5. Begin by setting the timer to 5 minutes. Then, adjust the speed control: start at a low speed (150 rpm) for about 15 seconds to balance the rotor and listen for any unusual sounds. If the operation is smooth and quiet, gradually increase the speed to approximately 300 rpm.
6. If any abnormal noise or vibration occurs during centrifugation, immediately reduce the speed to zero, switch off the power, and inform the TA .

Instruction for Using The Centrifuge-3

7. Once centrifugation is complete, reduce the speed to zero and wait until the centrifuge comes to a complete stop before opening the lid.
8. To separate the contents after centrifugation, use decantation to carefully pour off the supernatant, or use a pipette to extract the liquid layer, effectively separating the solids from the liquid.

7. Experimental Results

	6 M HCl	Boiling Water	0.5 M K_2CrO_4 6 M HOAc	15 M NH_3	6 M HNO_3
precipitate color					
solution color					
chemical formula of the main product					

8. Questions

1. **Why is concentrated hydrochloric acid not used as the reagent for forming chloride ions from cations? Please explain the reasons and provide the relevant chemical reaction equation.**

2. **Why does adding concentrated ammonia solution in step 1-4 dissolve AgCl(s), but adding nitric acid in step 1-5 precipitates AgCl(s)? Please explain the reasons and provide the relevant chemical reaction equations.**

3. The note in step 1-3 mentions that adding CH_3COOH to avoid other chromates. How does adding 1 drop of acetic acid prevent the precipitation of other chromates?

4. In step 1-3, if solution 1-2 contains Pb^{2+}, why continue using hot deionized water to extract precipitate 1-1?

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Chinese Version

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English Version:

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