Experiment 5 – Qualitative Analysis of Group I Cations

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I. Objective

To learn techniques for the separation and identification of common cations, in order to understand the equilibrium relationships involved in precipitation, dissolution, and the formation of complex ions.

II. Skills to be Acquired

- Usage of litmus paper and universal pH indicator paper
- Systematic analysis of cations
- Operation of centrifuge and identification techniques

III. Principles

(1) The Five Common Groups of Metal Cations

In chemical research, it is often necessary to analyze which metal elements are present in compounds or samples, or to further determine their concentrations. Before the development of modern analytical instruments such as atomic absorption spectrophotometers, simpler reagents and basic apparatus were used to perform systematic separation and identification of metal cations by applying principles of precipitation, dissolution, and complex ion formation equilibria.

Because qualitative analysis of cations has broad applications—including environmental or soil analysis and materials research—this experiment aims to teach basic techniques and analytical principles.

Qualitative analysis of cations is generally divided into three stages:

1. Cations are first separated into five groups based on their solubility properties using appropriate reagents.
2. Each group of cation precipitates is selectively dissolved and separated.
3. The presence of individual cations is confirmed through specific tests.

Cations are classified into five groups based on the solubility of their salts:

Group I Cations (Hg_2^{2+}, Ag^+, Pb^{2+}: insoluble chlorides):

- Only these three cations among common metal cations form insoluble chlorides with HCl(aq).
- When 6 M HCl is added to the solution, white precipitates of Hg_2Cl_2, AgCl, and $PbCl_2$ are formed, while the other metal cations remain in solution.

Group II Cations (Hg^{2+}, Pb^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, As^{3+}, Sb^{3+}, Sn^{4+}: sulfides insoluble in acidic solution):

- After removing Group I cations, adjust the pH of the solution to 0.5 and add H_2S. Under this acidic condition, the concentration of S^{2-} is very low, so only metal sulfides with very small solubility product constants (Ksp) will precipitate out, such as: **HgS, PbS, CuS, Bi_2S_3, CdS, As_2S_3, Sb_2S_3, SnS_2**.
- Metal cations with slightly larger Ksp, like **Zn^{2+} and Ni^{2+}**, will remain in the solution.

Group III Cations (**Al^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+}**; Sulfides or hydroxides insoluble in basic solution):

- After the removal of Group II sulfides from the acidic solution, the solution is adjusted to a slightly basic pH (around pH 8) and H_2S gas is introduced. Under this alkaline condition, the concentration of S^{2-} increases, allowing cations with larger Ksp values to form precipitates such as: **ZnS, NiS, CoS, MnS**.
- Due to the basic condition, **Al^{3+}, Fe^{3+}, Cr^{3+}** tend to form **hydroxide precipitates**, and are thereby separated as **$Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$**.

Group IV Cations (**Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}**; carbonate precipitates):

- These cations belong to Group IIA in the periodic table and share similar chemical properties.
- Their chlorides and sulfides are generally soluble, allowing them to remain in solution during separation of Groups I–III.
- In a mixed solution of **$(NH_4)_2CO_3/NH_4Cl/NH_3$**, they can be precipitated as **carbonates**

Group V Cations (**Na^+, K^+, NH_4^+**):

- These cations do not form precipitates during the separation steps of Groups I–IV and thus remain in the **final solution**.

Separation Flowchart Overview

- The separation flow of these five groups is illustrated in **Flowchart I**.
- This experiment will focus on the **systematic analysis and identification of Group I cations**.

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(2) Separation of Group I Metal Cations

Group I metal cations include **Hg_2^{2+}, Ag^+, and Pb^{2+}**.

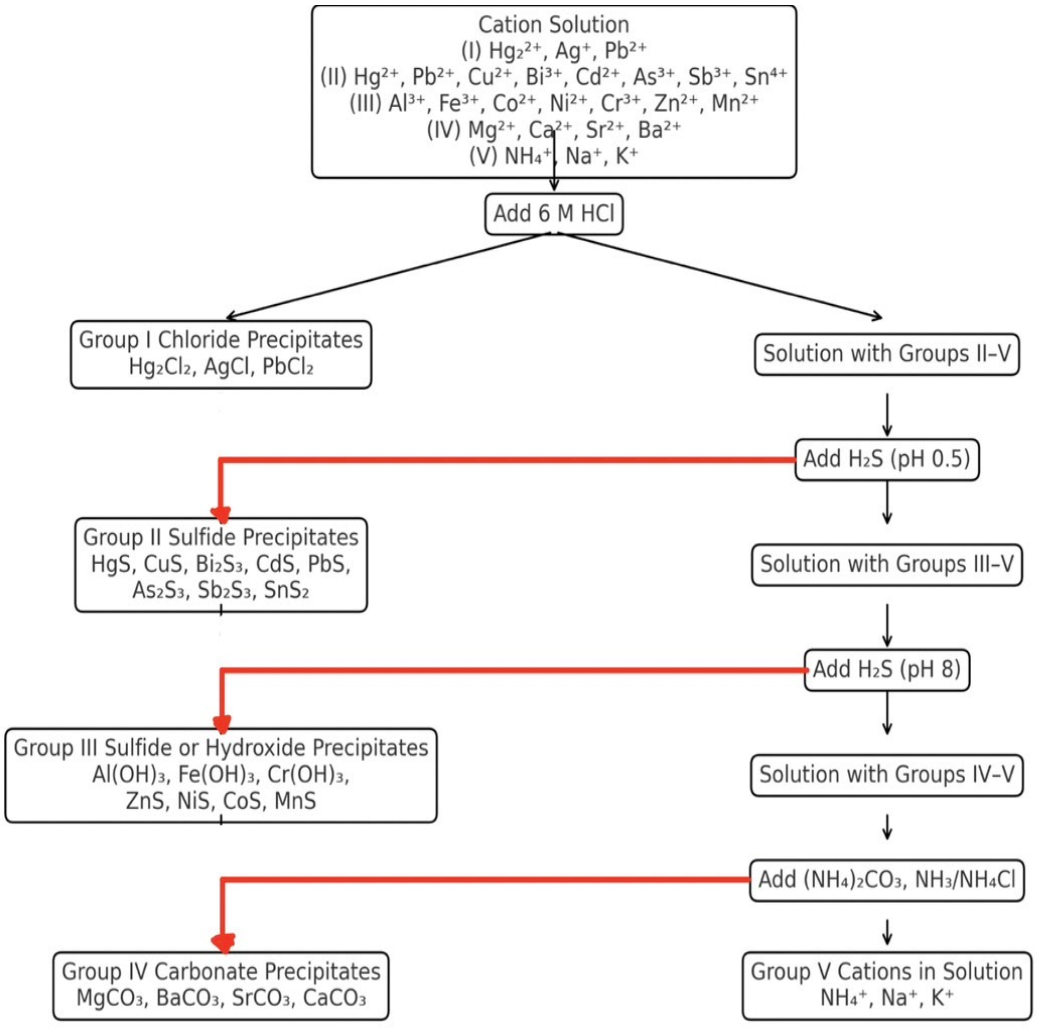
- They form **insoluble chlorides** when reacted with **HCl(aq)**, producing **white precipitates** of **Hg_2Cl_2, AgCl, and $PbCl_2$**.

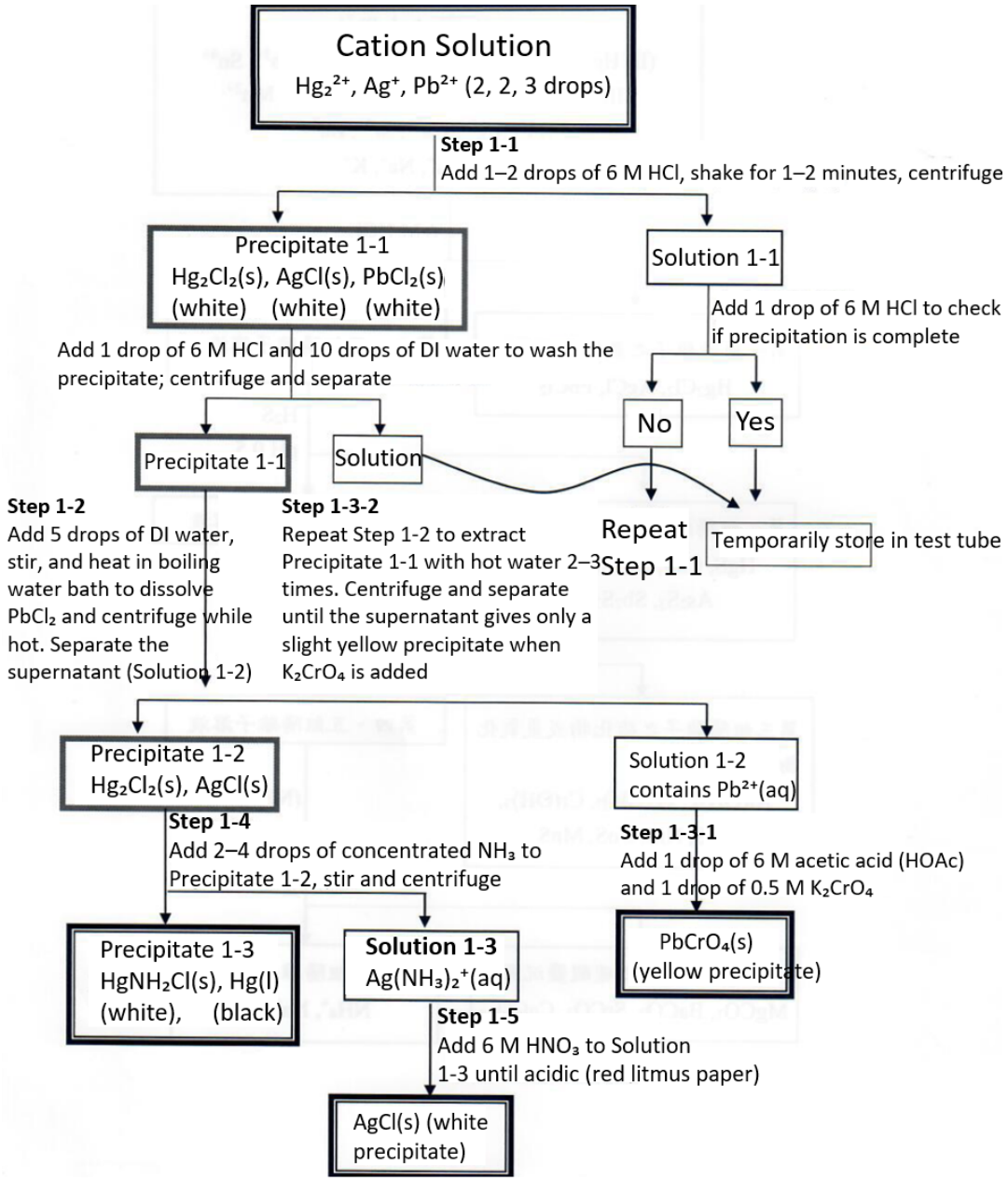
- Among them, **$PbCl_2$(s)** is more **soluble in hot water**, allowing it to be separated from the precipitate mixture by hot water extraction.
- This separates Pb^{2+} from the remaining precipitate of **AgCl(s)** and **Hg_2Cl_2(s)**.
- The remaining precipitate (AgCl and Hg_2Cl_2 mixture) can then be treated with **concentrated ammonia (NH_3)**:
  - **AgCl(s)** reacts with NH_3 to form the **soluble complex ion $Ag(NH_3)_2^+$**, as shown in Equation 5-1.
  - **Hg_2Cl_2(s)** undergoes a **disproportionation redox reaction** with NH_3 to produce a **black precipitate** mixture of **Hg(0)** and **$HgNH_2Cl$(s)**, as shown in Equation 5-2.
- This enables effective separation and identification of **Ag^+** and **Hg_2^{2+}**.
- **Equations:**

$$AgCl(s) + 2NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq) + Cl^-(aq) \quad \textbf{(5-1)}$$

$$Hg_2Cl_2(s) + 2NH_3(aq) \rightarrow Hg(0) + HgNH_2Cl(s) + NH_4^+(aq) + Cl^-(aq) \quad \textbf{(5-2)}$$

- **Flowchart I: Separation Process of Five Groups of Cations**





IV. Instruments and Materials:

Centrifuge	Droppers
Centrifuge tubes (5 pieces)	Glass stirring rods
Test tube brush	Beakers
Test tube rack	Blue litmus paper
Test tubes (10 pieces)	Latex gloves
Shared equipment:	
Electromagnetic hotplate stirrer	Test tube vortex mixer

V. Reagents:

(1) Standard Cation Solutions (10 mg cation/mL)	
Hg_2^{2+}: Mercury(I) nitrate dihydrate ($Hg_2(NO_3)_2 \cdot 2H_2O$)	
Ag^+: Silver nitrate ($AgNO_3$)	**Pb^{2+}**: Lead(II) nitrate ($Pb(NO_3)_2$)
(2) Other Reagents	
6 M HCl (hydrochloric acid)	**6 M HNO_3** (nitric acid)
0.5 M K_2CrO_4 (potassium chromate)	**6 M HOAc** (acetic acid, CH_3COOH)
Concentrated ammonia water, 15 M NH_3(aq)	

VI. Experimental Procedures:

Caution:

- This experiment involves handling concentrated acids and bases. Wear **latex gloves** at all times during the procedure.
- **Toxic acid fumes** may be produced. **All heating procedures**, including hot water baths, **must be performed inside a fume hood**.
- **Do not discard any precipitates or solutions** during the experiment. Keep them in test tubes until the entire procedure is finished and confirmed correct. Afterwards, **collect all waste for disposal in the heavy metal waste container**.

Step 1-1:

1. **Prepare the known mixture of cations:**
   Add **2 drops of Hg_2^{2+}**, **2 drops of Ag^+**, and **3 drops of Pb^{2+}** standard solutions into a single centrifuge tube.

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2. **Add 1 drop of 6 M HCl** into the centrifuge tube. Stir with a **glass rod** for 1–2 minutes. Let the mixture stand until precipitate settles. Then add **1 more drop of 6 M HCl** to check whether more white precipitate forms. If so, **continue adding dropwise until no further precipitate appears**.

Notes for Precipitation Step:

- **Note 1:** The precipitation of **$PbCl_2$** is relatively slow. You may use a **test tube vortex mixer** or gently **flick the centrifuge tube** with your finger to help ensure thorough mixing and complete precipitation.
- **Note 2:** Avoid adding too much **hydrochloric acid** (HCl), as excessive HCl may **redissolve the chlorides** due to complexation. Typically, **2–3 drops** are sufficient.

3. After **centrifuging** the precipitate (Precipitate 1-1) and solution, **decant** the clear supernatant into another centrifuge tube (Solution 1-1), and **add 1 drop of 6 M HCl** to check whether precipitation is complete.

   Note: Refer to lab skills training or demo videos for **centrifuge operation and decanting techniques**.

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4. **Washing the Precipitate:**

   Dilute **1 drop of 6 M HCl** with **10 drops of deionized water**.
   Use this diluted solution to **wash Precipitate 1-1**, then **centrifuge** again.
   The clear supernatant is then **decanted and combined into Solution 1-1**.

Step 1-2: Hot Water Extraction of $PbCl_2$

- Add **5 drops of deionized water** to Precipitate 1-1, stir well, and place in a **boiling water bath** for a few minutes.
- **Immediately centrifuge** and **transfer the clear supernatant** into another test tube (this becomes **Solution 1-2**).
- **Note:** If the solution is left too long and allowed to **cool**, **$PbCl_2$** will reprecipitate.

Step 1-3-1: Confirmation of Pb^{2+}

To **Solution 1-2**, add:

- **1 drop of 6 M acetic acid (CH_3COOH)**
- **1 drop of 0.5 M potassium chromate (K_2CrO_4)**
- If a **yellow precipitate** forms, this indicates the presence of **Pb^{2+}**.
- **Note:** Acetic acid is added to **prevent other chromates**, such as **$CuCrO_4$** or **$(BiO)_2CrO_4$**, from co-precipitating.

Solubility Products (Ksp):

- $PbCrO_4$: 2.8×10^{-13}
- $CuCrO_4$: 3.6×10^{-6}

Step 1-3-2: Repeated Hot Water Extraction

Extract Precipitate 1-1 **repeatedly with hot water** (typically **2–3 times**), until the **supernatant** yields only **slight turbidity** when **K_2CrO_4** is added.

Note: Incomplete removal of Pb^{2+} may interfere with **subsequent detection steps**.

Step 1-4: Testing for Mercury(I) (Hg_2^{2+})

1. After multiple hot water extractions of **Precipitate 1-1**, the remaining **white solid** is **Precipitate 1-2**, which no longer contains **Pb^{2+}**.
2. Add **2–4 drops of concentrated ammonia (15 M NH_3)** to **Precipitate 1-2**, and stir using a glass rod to disperse the solid.

3. After **centrifugation**, transfer the **clear supernatant** to another test tube (this becomes **Solution 1-3**) and **observe the color** of the remaining precipitate (**Precipitate 1-3**).
4. If a **black precipitate** forms (a mixture of **$HgNH_2Cl$(s)** and elemental **Hg(0)**), this confirms the presence of **Hg_2^{2+}**.
5. **Note:** If **Pb^{2+}** is not completely removed, **white $Pb(OH)_2$(s)** may form upon adding ammonia, which could interfere with detection.

Step 1-5: Testing for Silver Ion (Ag^+)

1. Add **6 M nitric acid (HNO_3)** drop by drop to **Solution 1-3**, stirring thoroughly after each addition, until the solution becomes **acidic**.
2. If a **white precipitate** appears, it indicates the presence of **Ag^+**.
3. **Note:** Use a glass rod to transfer a drop of solution onto **blue litmus paper** to test acidity. Blue litmus turns **red** when acidic.

Step 1-6: Finalization

1. At the end of the experiment, **retain all separated and identified precipitates** along with your lab notes. Submit them **together to the TA for verification**.
2. Identified ions: **Pb^{2+}**, **Hg_2^{2+}**, **Ag^+**
3. **All waste liquids contain heavy metals** and must be **disposed of in the designated heavy metal waste container**.
4. Clean all used **glassware**, and **remove any labels** from test tubes and centrifuge tubes.

VII. References:

1. This material is translated from 大學普通化學實驗（第 15 版）University General Chemistry Lab, 15th ed.，國立臺灣大學出版中心。
2. King, E. J. *Qualitative Analysis and Electrolytic Solutions*; Harcourt, Brace: New York, 1976.
3. 張苔旭，《分析化學基礎》；藝軒：台北市，1989，第 213 頁。
4. 鄭華生，《無機半微量分析原理和實驗》第七版；狀元：台北市，1985，第 115 頁。
5. 曾國輝，《化學（第二版）》；藝軒：台北市，1989，第 1097 頁。

Experiment 5 – Qualitative Analysis of Group I Cations

Name: _____ **Student ID:** _____

Department: _____ **Group:** _____ **Date:** _____

I. Experimental Results

1. Record the qualitative identification results of the mixed cation solution (including: formation of precipitate or dissolution, color change, and chemical equation of the product) in the table below:

Step/Result	**1-1** (6 M HCl)	**1-2** (Boiling Water)	**1-3** (0.5 M K_2CrO_4 + 6 M HOAc)	**1-4** (Conc. NH_3)	**1-5** (6 M HNO_3)
Precipitate Color					
Solution Color					
Major Products & Chemical Equations					

II. Questions and Discussion

1. Look up the solubility product constants (**Ksp**) of **Hg_2Cl_2**, **AgCl**, and **$PbCl_2$**. State the sources of your references and write out the corresponding **equilibrium expressions**.

2. When testing an unknown cation solution in this experiment, a white precipitate forms upon the addition of an appropriate amount of **6 M HCl**. After separating the precipitate by centrifugation and adding **5 drops of concentrated ammonia** to it, the precipitate turns **black**. Based on this observation, **which metal cation(s)** are likely present in this unknown solution? Write the **chemical equilibrium equations** involved in this detection process.