Experiment 6

QUALITATIVE ANALYSIS OF CATION GROUP 2

Introduction

Group 2 cations react with $\text{H}_2\text{S}$ in 0.1 to 0.3 M hydrochloric acid solution to form insoluble sulfides, namely $\text{HgS}$, $\text{PbS}$, $\text{Bi}_2\text{S}_3$, $\text{CuS}$, $\text{CdS}$, $\text{As}_2\text{S}_3$, $\text{SnS}_2$, and $\text{Sb}_2\text{S}_3$. The first five cations ($\text{Hg}^{2+}$, $\text{Pb}^{2+}$, $\text{Bi}^{3+}$, $\text{Cu}^{2+}$, $\text{Cd}^{2+}$) belong to the copper subgroup. Their sulfides are not acidic and thus are insoluble in KOH solution. The last three cations ($\text{As}^{3+}$, $\text{Sn}^{4+}$, $\text{Sb}^{3+}$) belong to the arsenic subgroup, which form acidic sulfides that are soluble in KOH and thus separable from the copper subgroup. Since group 2 cations are numerous and many are toxic, we will only examine a mixture of $\text{Cu}^{2+}$, $\text{Bi}^{3+}$, $\text{Sn}^{4+}$, and $\text{Sb}^{3+}$ ions in this experiment.
Flow chart: Separation and identification of cation group 2

Cations solution
\( \text{Cu}^{2+}, \text{Bi}^{3+}, \text{Sb}^{3+}, \text{Sn}^{4+} (2, 2, 2, 8 \text{ drops}) \)

Step 2-1
Add 2 d 13\%TA, warm in water bath, cfg.

\[\text{Ppt 2-1} \]
\( \text{Bi}_2\text{S}_3, \text{CuS}, \text{Sb}_2\text{S}_3, \text{Sn}_2\text{S}_2 \)

Step 2-2
Rinse ppt with 1 d 6 M \( \text{NH}_4\text{Cl} \) and 20 d water, cfg.
Add 10 d 0.5 M KOH to ppt, mix well.
Heat in boiling water bath (5 min), cfg.
Repeat this extraction with KOH one more time.

\[\text{Soln 2-1} \]

Repeat step 2-1 till pptn is complete, discard liquid.

Waste container

Step 2-3
Wash ppt with 1 d 0.2 M \( \text{NH}_4\text{NO}_3 \) and 20 d water, cfg.
Add 5 d 6 M \( \text{HNO}_3 \), 5 d water into ppt, heat in boiling water bath.
After rxn is complete (effervescence observed), cfg.

\[\text{Ppt 2-2 (Cu subgroup)} \]
\( \text{Bi}_2\text{S}_3, \text{CuS} \)

Step 2-4
Add 15 M \( \text{NH}_3 \) till basic (confirm with litmus test), cfg.

\[\text{Soln 2-3} \]
\( \text{Bi}^{3+}, \text{Cu}^{2+} \)

Discard residue.

Step 2-5
Add sodium stannite reagent (freshly prepared).

\[\text{Ppt 2-4} \]
\( \text{Bi(OH)}_3(s) \)

Step 2-6
Add ca. 20 d 12 M \( \text{HCl} \), heat in boiling water bath till ppt dissolves.
Cfg, pour supernatant into evaporating dish.

\[\text{Soln 2-4} \]
\( \text{Cu(NH}_3)_2^{2+} \) (deep blue)

Step 2-7
Heat, allow to evaporate till approx 4 d left.
Add 1 mL \( \text{H}_2\text{O} \), divide to 2 portions.

\[\text{Sb test} \]

Step 2-8
Add 1/4 small spatula \( \text{H}_2\text{C}_2\text{O}_4(s) \), 2 d 13\%TA.
Heat in hot water bath.

\[\text{Sb}_2\text{S}_3(s) \text{ (orange)} \]

Step 2-9
Add Al strip and 10 d 6 M \( \text{HCl} \), heat in water bath till dissolves, cfg.
Add 2 d 0.1 M \( \text{HgCl}_2 \) to liquid portion.

\[\text{Sn test} \]

Step 2-10

\[\text{Hg}_2\text{Cl}_2(s), \text{Hg}^0 \text{ (off-white)} \]
**Apparatus**
Hot plate, vortex mixer, centrifuge, centrifuge tubes (5), evaporating dish, crucible tongs, test tube holder, test tubes (10), test tube rack, glass rod, beaker, dropper, latex gloves, litmus paper, and universal indicator paper.

**Chemicals**

I. **Standard cation solutions (10 mg ion/mL)**
- Bi^{3+}: bismuth(III) nitrate pentahydrate, Bi(NO_3)_3·5H_2O
- Cu^{2+}: copper(II) nitrate trihydrate, Cu(NO_3)_2·3H_2O
- Sb^{3+}: antimony(III) chloride, SbCl_3
- Sn^{4+}: tin(IV) chloride pentahydrate, SnCl_4·5H_2O

II. **Test reagents**
- Aluminum, Al
- Oxalic acid, H_2C_2O_4
- 13% Thioacetamide, CH_3CSNH_2
- Concentrated ammonia water, 15 M NH_3(aq)
- Concentrated hydrochloric acid, 12 M HCl(aq)
- 6 M Hydrochloric acid, HCl(aq)
- 6 M Ammonium chloride, NH_4Cl
- 0.2 M Ammonium nitrate, NH_4NO_3
- 0.1 M Mercury(II) chloride, HgCl_2
- 0.5 M Potassium hydroxide, KOH
- 6 M Nitric acid, HNO_3(aq)
- 0.2 M Tin(II) chloride, SnCl_2
- 6 M Sodium hydroxide, NaOH

**Procedure**

★ Wear latex gloves while performing the experiment.
★ This experiment produces toxic and acidic fumes. All heating should be carried out in the fume hood.
★ The liquid waste of this experiment contains heavy metals. It should be disposed properly in the liquid waste container.

<table>
<thead>
<tr>
<th>Step</th>
<th>Procedure</th>
<th>Illustration</th>
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<tr>
<td>2-1</td>
<td>1. Preparation of a known solution: Add 2 drops each of Bi^{3+}, Cu^{2+}, Sb^{3+} and 8 drops of Sn^{4+} standard solution to a centrifuge tube.</td>
<td><img src="image1.jpg" alt="Illustration" /></td>
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</tbody>
</table>
2. Test the pH value of the mixed cations solution using universal indicator paper.

Note 1: To separate group 2 cations from group 3 cations, the pH of solution should be acidic ([H⁺] = 0.1~0.3 M) to keep [S²⁻] low enough, thereby preventing the precipitation of group 3 cations sulfides, which have higher K_{sp} values. However, the pH must not be too low. Since high [H⁺] results in low [S²⁻], it prevents complete precipitation of group 2 cations sulfides.

Note 2: Since the prepared group 2 cations known solution is acidic and contains no group 3 cations, we skip adjusting pH value of solution.

3. Add 2 drops of 13% thioacetamide solution (abbreviated TA) to the group 2 cations solution and heat the solution in a warm water bath until brown to black precipitate appears.

Note: Thioacetamide undergoes hydrolysis in an acidic or basic solution to form H₂S.

\[
\begin{align*}
\text{CH₃CNH₂} + \text{H}^+ + 2\text{H}_2\text{O} &\xrightarrow{\Delta} \text{CH₃COH} + \text{NH}_4^+ + \text{H}_2\text{S} \\
\end{align*}
\]

4. Centrifuge and decant the supernatant into another centrifuge tube (solution 2-1). The residue is precipitate 2-1. Add 2 more drops of TA to the solution, and then heat in a water bath and centrifuge again.

5. Then add 2 drops of TA and heat again. If any precipitate is formed, repeat the procedure until the precipitation of cations is complete.

Note: We usually conduct the precipitation steps for three times.
| 2-2  | 1. Rinse the residue twice with 1 drop of 6 M NH₄Cl and 20 drops of hot water. Combine the washing solution and centrifuge. Combine all precipitates and discard the supernatant.  
Note: Washing solution contains strong electrolyte (NH₄Cl) to prevent the formation of colloidal sulfides.  
2. Add 10 drops of 0.5 M KOH to precipitate 2-1, mix thoroughly, and heat in a boiling water bath for a few minutes.  
3. Centrifuge and decant the supernatant into another centrifuge tube (solution 2-2) and reserve it for the test in step 2-6. The residue is precipitate 2-2.  
4. Repeat the extraction with a second portion of KOH solution. Centrifuge and combine the supernatant with solution 2-2. |
| 2-3  | 1. Wash precipitate 2-2 twice with 1 drop of 0.2 M NH₄NO₃ and 20 drops of hot water.  
2. Centrifuge and discard the supernatant, and then add 5 drops each of water and 6 M HNO₃. Heat in a boiling water bath until the reaction occurs.  
Note: There will be no visible change at the beginning of heating, but bubbling will be observed later, resulting from NO₂ gas produced by the reaction of precipitated sulfides and nitric acid.  
3. Centrifuge and transfer the supernatant (solution 2-3) into a clean centrifuge tube.  
Note: Precipitate 2-2 should dissolve completely in nitric acid. A small amount of cloudy, milky-white suspension is due to elemental sulfur produced by the reaction. |
1. Add concentrated ammonia water (15 M) to solution 2-3 until it is alkaline.
   Note: Check with litmus paper.

2. Centrifuge even though you see no precipitate. Collect the small amount of residue (precipitate 2-4). The supernatant is solution 2-4. The presence of Cu$^{2+}$ in solution 2-4 is verified by the deep blue color of Cu(NH$_3$)$_4^{2+}$.
   Note: Gelatinous precipitate of Bi(OH)$_3$ is hard to see, particularly when suspended in a blue solution.

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1. Preparing sodium stannite reagent:
   Add 3 drops of SnCl$_2$ solution to a test tube, and then add 6 M NaOH dropwise with careful mixing until the precipitate of Sn(OH)$_2$ re-dissolves. Use the freshly prepared solution immediately.

2. Add freshly prepared sodium stannite reagent to precipitate 2-4.
3. The presence of Bi$^{3+}$ is indicated by the immediate formation of Bi metal (black deposit).

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1. Add concentrated hydrochloric acid (12 M) to solution 2-2 drop by drop. Stir and mix the solution to observe the formation and subsequent dissolution of precipitated sulfides. Heat in a hot water bath to complete the reaction.
   Note: After heating, Sb$_2$S$_3$ and SnS$_2$ should form complexes (SnCl$_6^{2-}$, SbCl$_4^-$) and dissolve completely.

2. Centrifuge and pour the supernatant into an evaporating dish (solution 2-5). Discard the residue.
| 2-7 | 1. In fume hood, heat and evaporate solution 2-5 slowly to half the original volume, or not less than 4 drops remaining.  
Note: If evaporation is carried too far, some SnCl$_4$ may be lost. | ![Image](image1.png) |
| 2-8 | 2. Place the evaporating dish on the fume hood benchtop and dilute with 1 mL DI water. Divide the solution into one test tube and one centrifuge tube. Perform the Sn and Sb tests below separately. | ![Image](image2.png) |
| 2-9 | **Sb test**  
1. Add 1/4 spatula of solid H$_2$C$_2$O$_4$ and 2 drops of TA to the solution.  
2. Warm it in a hot water bath. The formation of an orange Sb$_2$S$_3$ precipitate confirms the presence of Sb$^{3+}$.  
Note: C$_2$O$_4^{2-}$ and Sn$^{4+}$ form a stable Sn(C$_2$O$_4$)$_3^{2-}$ complex, so it will not obscure the formation and color of Sb$_2$S$_3$ precipitate. | ![Image](image3.png) |
| 2-9 | **Sn test**  
1. Add a small aluminum strip (5 mm) and 10 drops of 6 M HCl to the solution. Heat in a hot water bath to dissolve the aluminum.  
Note: Al can reduce Sn$^{4+}$ and Sb$^{3+}$ to Sn$^{2+}$ and Sb in acidic solution.  
\[
\text{SbCl}_4^{-} (aq) + \text{Al(s)} \rightarrow \text{Sb(s)} + \text{Al}^{3+} (aq) + 4\text{Cl}^{-} (aq) \\
3\text{SnCl}_6^{2-} (aq) + 4\text{Al(s)} \rightarrow 3\text{Sn(s)} + 4\text{Al}^{3+} (aq) + 18\text{Cl}^{-} (aq) \\
\text{Sn(s)} + 2\text{H}^{+} (aq) \rightarrow \text{Sn}^{2+} (aq) + \text{H}_2(g)
\] | ![Image](image4.png) |
2. Centrifuge. A black precipitate may indicate the presence of Sb$^{3+}$.
3. Remove the precipitate and dilute the supernatant with an equal volume of water.

4. Without delay, add 2 drops of HgCl$_2$ solution. The formation of a white to gray precipitate (Hg$_2$Cl$_2$, Hg) proves the presence of Sn$^{2+}$ ion.

   Note: Since Sn$^{2+}$ is oxidized by atmospheric oxygen, the HgCl$_2$ solution should be added as soon as possible.

2-10

1. Keep and present the identification products to lab instructor when finishing the experiment.
2. The liquid waste containing heavy metals should be collected and discarded into the recycling container.

References