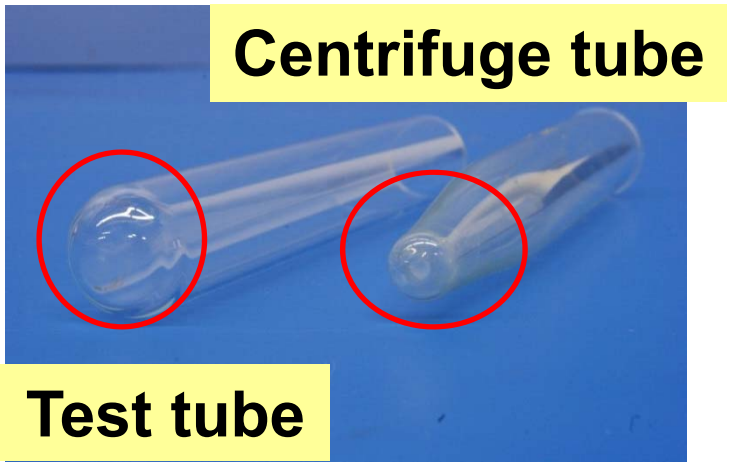
Qualitative Analysis of Group II Cations

(2016/03/03 revised)

Collect:

- 5 centrifuge tubes
- Labels
- Evaporating dish
- Latex gloves
- Two droppers
- Test tube holder and crucible tongs



Prepare:

- Test tube rack, test tubes, and beaker
- Take out centrifuge

***Conc. NH_3(aq) and HCl: in hood**

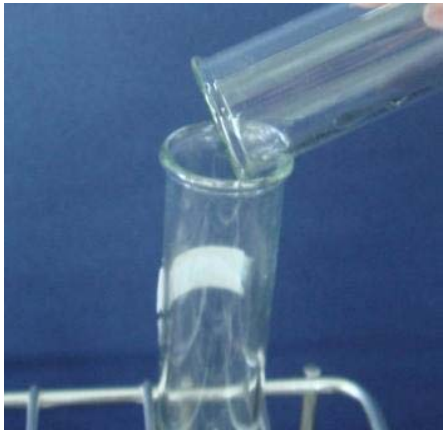
Objective

- To learn the techniques of separating and identifying some common cations
- To understand the principles of precipitation and equilibrium of complex formation

Techniques

- Vortex mixer
- Precipitation
- Centrifuge
- Decantation
- Litmus and universal indicator paper

Vortex Mixer



Decantation

Introduction: Qualitative Analysis of Group I~V Cations

Cationic Solutions

(I) Insoluble chlorides: Hg_2^{2+}, Ag^+, Pb^{2+}

(II) Insoluble sulfides in acidic medium: Hg^{2+}, Pb^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, As^{3+}, Sb^{3+}, Sn^{4+} (**metallic sulfide precipitates with smaller K_{sp}**)

(III) Insoluble sulfide or hydroxides in alkaline medium: Al^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+} (**metallic sulfide precipitates with greater K_{sp}**)

(IV) Insoluble Carbonates: Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}

(V) Soluble cations: NH_4^+, Na^+, K^+

Group 2 Cations - Copper and Arsenic Subgroup

Group 2 cations – Insoluble sulfides in acidic medium

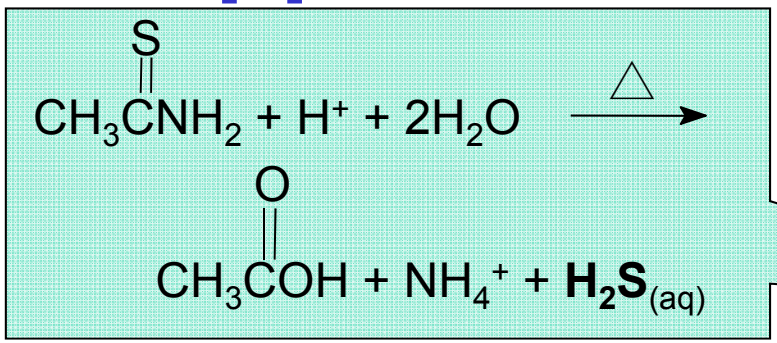
– **HgS, PbS, CuS, Bi_2S_3, CdS**, As_2S_3, Sb_2S_3, SnS_2

- **Copper subgroup** – **Hg^{2+}, Pb^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}**
  The sulfides are **insoluble in KOH** solution, only **soluble in nitric acid**

- **Arsenic subgroup – As^{3+}, Sb^{3+}, Sn^{4+}**
  The sulfides are thioamphoteric that are **soluble in KOH(aq) and nitric acid**

- **Mostly are toxic heavy metals**
  thus we only examine **Cu^{2+}, Bi^{3+}, Sb^{3+}, Sn^{4+}**

Flow Chart for Separating Copper and Arsenic Subgroups



Cationic Solution
Cu^{2+}, Bi^{3+}, Sb^{3+}, Sn^{4+}
(2, 2, 2, 8 drops)

(pH 0.5)
2 d 13%TA, Δ
Centrifuge and separate
(Repeat 13%TA precipitation once)

Ppt 2-1
Bi_2S_3, CuS, Sb_2S_3, SnS_2

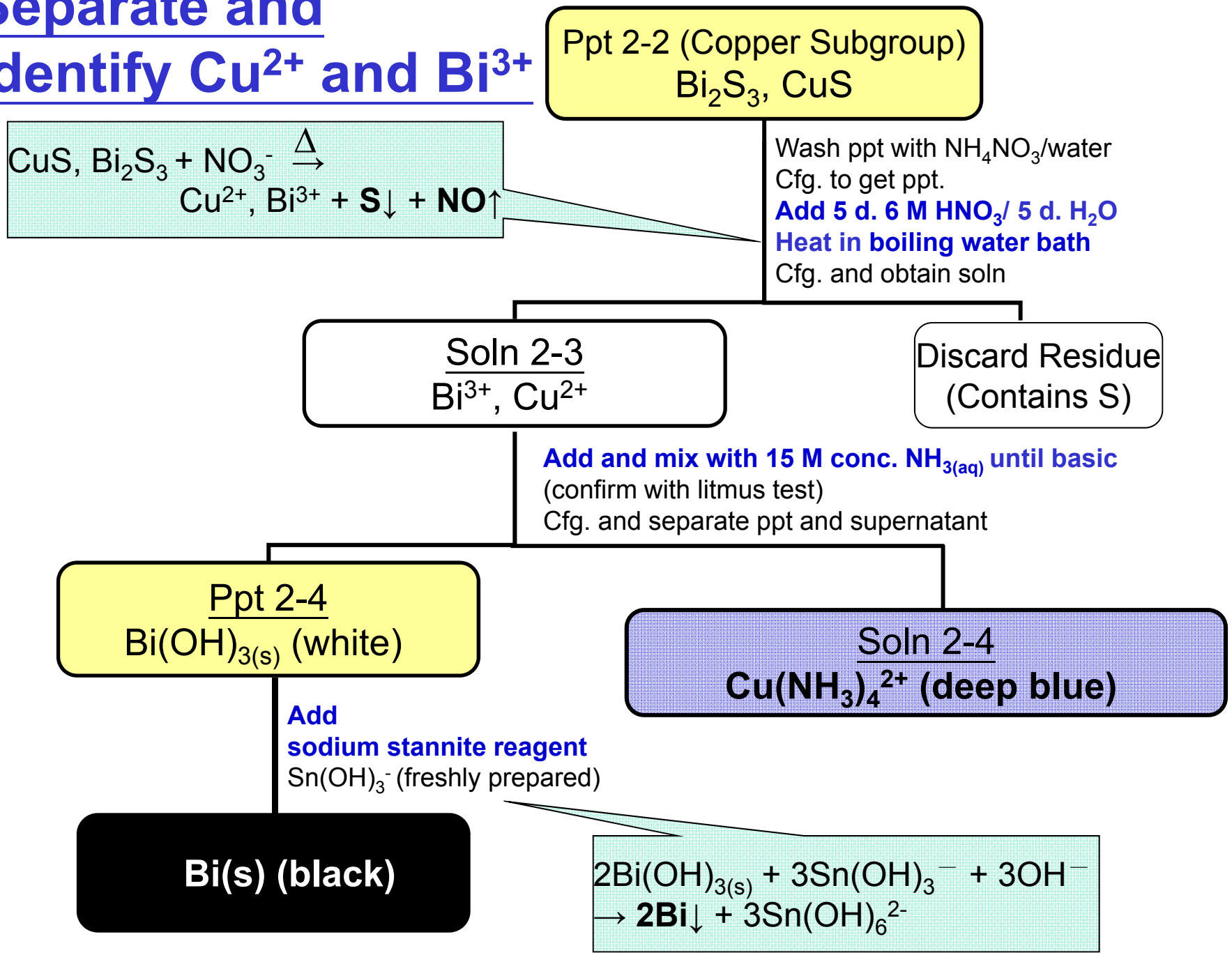
Soln 2-1

Wash ppt with 1 d 6 M NH_4Cl and 20 d of water, cfg.
Add 10 d 0.5 M KOH to ppt and mix well
Heat in boiling water bath
Cfg. and separate the ppt and supernatant
(Repeat this extraction with KOH once)

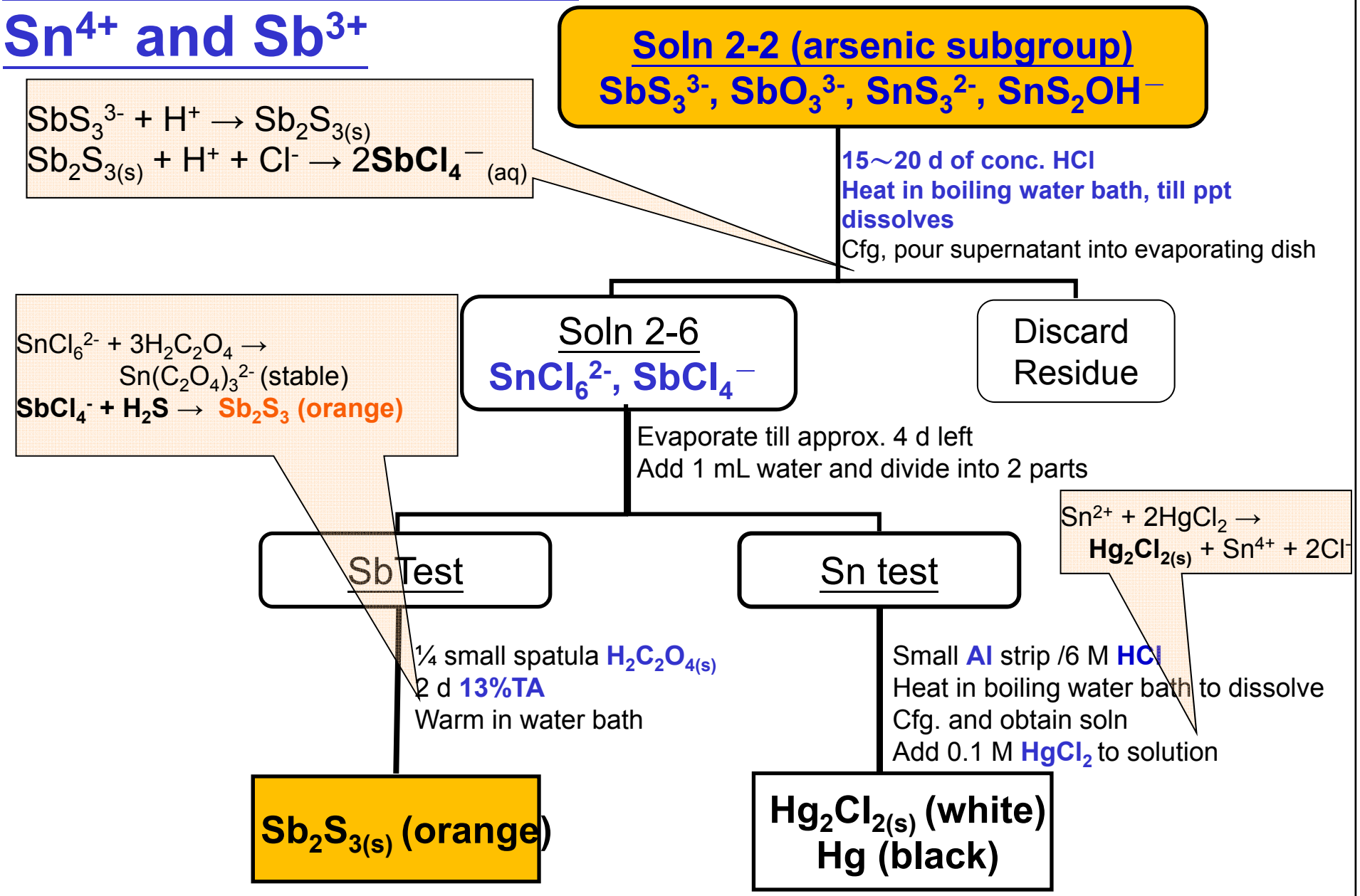
Ppt 2-2 (copper subgroup)
Bi_2S_3, CuS

Soln 2-2 (arsenic subgroup)
SbS_3^{3-}, SbO_3^{3-}, SnS_3^{2-}, SnS_2OH^-, (KOH)

Separate and Identify Cu^{2+} and Bi^{3+}



Separate and Identify Sn^{4+} and Sb^{3+}



Separate Copper and Arsenic Subgroups

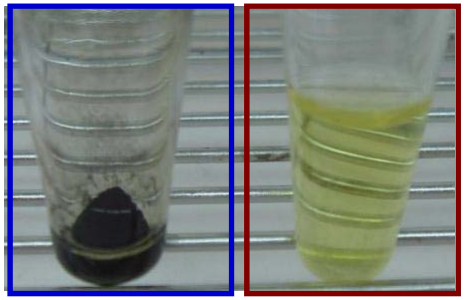
- **Add 13%TA**
- Heat in warm water
- Produce sulfide ppt

- Centrifuge
- Balance diagonally

- Separate ppt and supernatant by decantation

Sulfide ppt

1) 1 d 6 M NH_4Cl/20 d H_2O to wash ppt, then cfg.
2) **Add 10 d 0.5 M KOH to ppt**
3) **Heat in boiling water bath**
4) Cfg. and separate
5) Repeat KOH extraction once

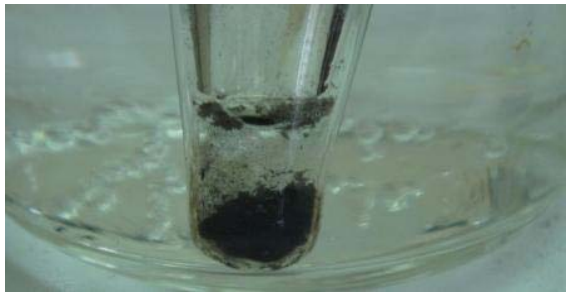


Ppt 2-2
Copper subgroup
CuS, Bi_2S_3

Soln 2-2
Arsenic subgroup
Contains Sn^{4+}, Sb^{3+}

Copper Subgroup: Use HNO_3 to Dissolve CuS, Bi_2S_3

Ppt 2-2
Copper subgroup
CuS, Bi_2S_3



- 1 d 0.2 M NH_4NO_3/20 d H_2O to wash ppt,
- Cfg. to get ppt.

- **Add 5 d water and 5 d 6 M HNO_3**
- Heat in boiling water bath

- Heat till reaction starts (starts to bubble)
- Ppt is dissolved and appears white and milky

$$3(CuS, Bi_2S_3)_{(s)} + 2NO_3^-{}_{(aq)} + 8H^+{}_{(aq)} \rightarrow$$
$$3(Cu^{2+}、Bi^{3+})_{(aq)} + \mathbf{\underline{2NO}_{(g)}}\uparrow + \mathbf{3S}\downarrow + 4H_2O$$

- The water bath should be keep boiling
- Mix the HNO_3 and ppt thoroughly
- Heat to the black sulfides disappear, and the solution appears to be off-white for elemental sulfur forms

Separate and Identify Cu^{2+} and Bi^{3+}

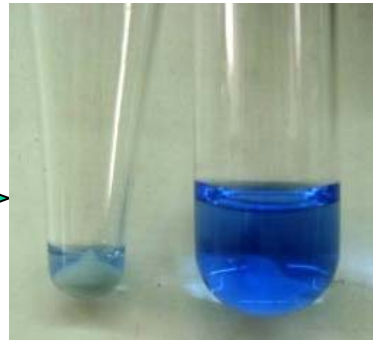
Cfg. and take supernatant

Contains Cu^{2+}, Bi^{3+}

Add conc. NH_3 to basic

(confirm with litmus test)

Centrifuge



$Cu(NH_3)_4^{2+}$

Add sodium stannite reagent*

Bi

*Prepare sodium stannite reagent freshly :

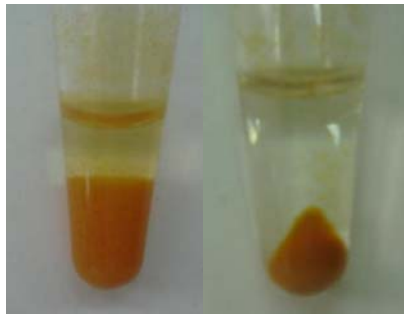
$$SnCl_{2(aq)} \xrightarrow{NaOH_{(aq)}} Sn(OH)_{2(s)} \xrightarrow{NaOH_{(aq)}} Sn(OH)_{3(aq)}^{-}$$

Do not add more NaOH when ppt dissolved

Separate and Identify Sn^{4+} and Sb^{3+}

Soln 2-2
Contains
Sn^{4+}, Sb^{3+}

Add conc. HCl slowly



Excess conc. HCl (ca. 15-20 d)

Dissolve when heated
Transfer to evaporating dish

$SbS_3^{3-} + SbO_3^{3-} + 6H^+ \rightarrow \mathbf{Sb_2S_{3(s)}(orange)} + 3H_2O$

$SnS_2OH^- + H^+ \rightarrow \mathbf{SnS_{2(s)}(yellow)} + H_2O$

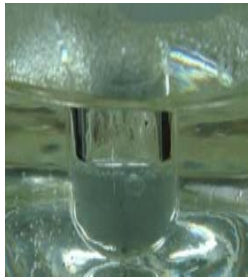
Evaporate to 4 d

- Add 1 mL H_2O
- Separate into 2 tubes

- 1/4small spatula $\mathbf{H_2C_2O_{4(s)}}$
- 2 d **13%TA**
- Heat in water bath

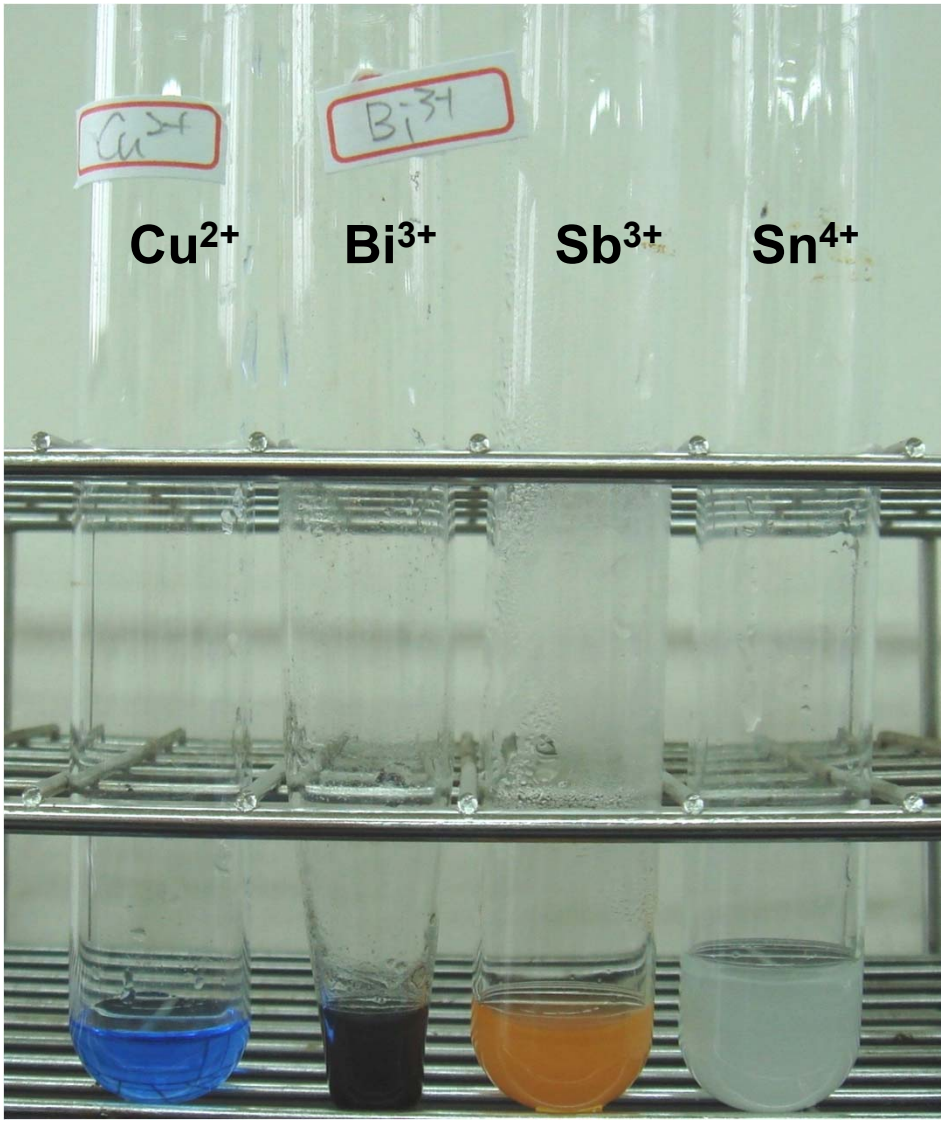
Sb

- Small **Al** strips / **HCl**
- Heat till dissolve,
- Cfg. to get soln
- Add $\mathbf{HgCl_2}$ to liquid portion



Sn

Expected Results



- Keep the resulting solutions for TA to check
- Record all the observations, i.e. color, ppt, rate etc.

Manipulate the Centrifuge

- Use centrifuge tubes in centrifuge, **do not use test tubes**
- Centrifuge tubes should be placed in **opposite sides to keep balanced**
- The lid should be closed during use; the centrifuge should be started from **slow** to check if there are unusual sounds, then the speed can be increased
- If there are unusual sounds or movement in the centrifuge, the power should be turned off first to fix
- There must be at least one person watching the centrifuge when in use
- Centrifuge for approx. **1~2 min**, open lid when the centrifuge has completely stopped

Notice

- Wear gloves
- Always use test tube holders, test tube racks, and crucible tongs
- Add reagents on top of the centrifuge tube to avoid contamination of chemicals
- Do not take excess chemicals to avoid pollution
- Solutions must be mixed thoroughly after adding reagents
- Dip solution on testing paper to determine acidity
- All heating should be done in the hood
- Conc. NH_3(aq) and HCl(aq) are in hood
- Recycle heavy metal waste