Experiment 4

QUALITATIVE ANALYSIS OF GROUP 2 CATIONS

Objective

The purpose of this experiment is to learn the techniques to separate and identify group 2 cations which produce insoluble sulfides in an acidic solution, and to understand the principles for the equilibria of precipitation and complex formation.

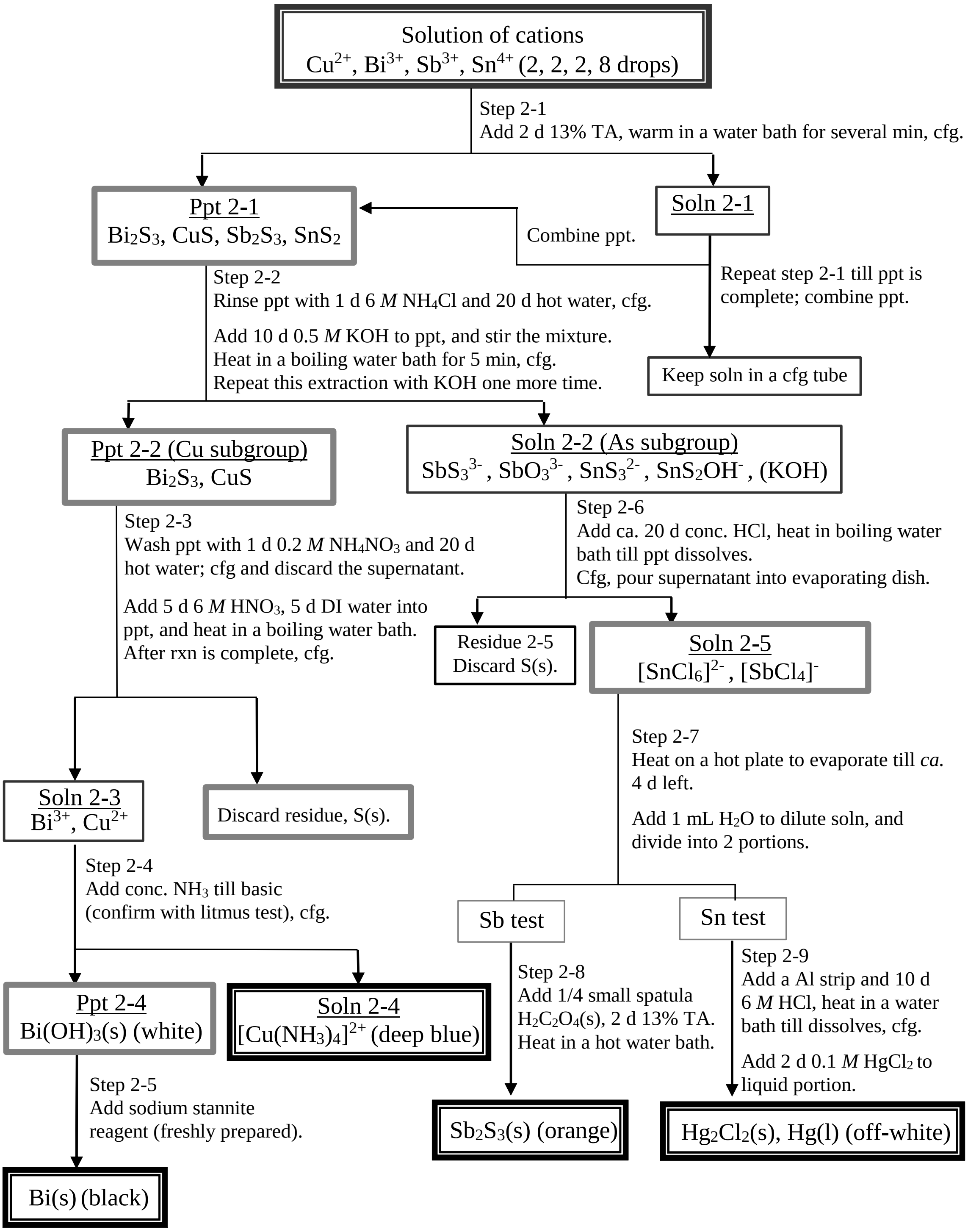
Lab techniques

- Using litmus and universal indicator paper
- Operating the stirrer/hot plate, centrifuge, and vortex mixer

Introduction

Group 2 cations react with H_2S(aq) in a pH 0.5 acidic solution (0.1 to 0.3 *M* hydrochloric acid) to form insoluble sulfides, namely HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, SnS_2, and Sb_2S_3. The first five cations (Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}) belong to the copper subgroup, whose sulfides are soluble in nitric acid but insoluble in KOH solution. The last three cations (As^{3+}, Sn^{4+}, Sb^{3+}) belong to the arsenic subgroup, which forms amphoteric sulfides that are soluble in both nitric acid and KOH solution and thus separable from the copper subgroup. Since group 2 cations are numerous and many of them are rather toxic, we will only examine a mixture of Cu^{2+}, Bi^{3+}, Sn^{4+}, and Sb^{3+} ions in this experiment. The analysis and identification processes are shown in the flow chart for the analysis of group 2 cations.

Flow Chart for the Analysis of Group 2 Cations



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

Step 2-1
Add 2 d 13% TA, warm in a water bath for several min, cfg.

Soln 2-1

Repeat step 2-1 till ppt is complete; combine ppt.

Keep soln in a cfg tube

Combine ppt.

Ppt 2-1
Bi_2S_3, CuS, Sb_2S_3, SnS_2

Step 2-2
Rinse ppt with 1 d 6 *M* NH_4Cl and 20 d hot water, cfg.

Add 10 d 0.5 *M* KOH to ppt, and stir the mixture.
Heat in a boiling water bath for 5 min, cfg.
Repeat this extraction with KOH one more time.

Ppt 2-2 (Cu subgroup)
Bi_2S_3, CuS

Step 2-3
Wash ppt with 1 d 0.2 *M* NH_4NO_3 and 20 d hot water; cfg and discard the supernatant.

Add 5 d 6 *M* HNO_3, 5 d DI water into ppt, and heat in a boiling water bath.
After rxn is complete, cfg.

Soln 2-3
Bi^{3+}, Cu^{2+}

Discard residue, S(s).

Step 2-4
Add conc. NH_3 till basic (confirm with litmus test), cfg.

Ppt 2-4
$Bi(OH)_3$(s) (white)

Soln 2-4
$[Cu(NH_3)_4]^{2+}$ (deep blue)

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

Bi(s) (black)

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

Step 2-6
Add ca. 20 d conc. HCl, heat in boiling water bath till ppt dissolves.
Cfg, pour supernatant into evaporating dish.

Residue 2-5
Discard S(s).

Soln 2-5
$[SnCl_6]^{2-}$, $[SbCl_4]^-$

Step 2-7
Heat on a hot plate to evaporate till *ca.* 4 d left.

Add 1 mL H_2O to dilute soln, and divide into 2 portions.

Sb test

Step 2-8
Add 1/4 small spatula $H_2C_2O_4$(s), 2 d 13% TA.
Heat in a hot water bath.

Sb_2S_3(s) (orange)

Sn test

Step 2-9
Add a Al strip and 10 d 6 *M* HCl, heat in a water bath till dissolves, cfg.

Add 2 d 0.1 *M* $HgCl_2$ to liquid portion.

Hg_2Cl_2(s), Hg(l) (off-white)

Abbreviations:
TA: thioacetamide

Apparatus

Centrifuge, centrifuge tube (6), rubber septum (2), evaporating dish, crucible tongs, test tube holder, test tube (10), test tube rack, glass rod, dropper, NBR gloves, litmus paper, and universal indicator paper.
Shared: stirrer/hot plate, beaker (400 mL), and vortex mixer.

Chemicals (*Indicate the properties of chemicals in the pre-lab report)

I. Standard cation solutions (10 mg ion/mL)

Bi^{3+}: bismuth(III) nitrate pentahydrate*, $Bi(NO_3)_3 \cdot 5H_2O$
Cu^{2+}: copper(II) nitrate trihydrate*, $Cu(NO_3)_2 \cdot 3H_2O$
Sb^{3+}: antimony(III) chloride*, $SbCl_3$
Sn^{4+}: tin(IV) chloride pentahydrate*, $SnCl_4 \cdot 5H_2O$

II. Test reagents

Aluminum, Al
Oxalic acid*, $H_2C_2O_4$
13% Thioacetamide*, CH_3CSNH_2
Concentrated ammonia water, 15 *M* $NH_3(aq)$
6 *M* and concentrated hydrochloric acid, 12 *M* $HCl(aq)$
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*, $SnCl_2 \cdot 2H_2O$
6 *M* Sodium hydroxide, NaOH

Procedure

★ Put the NBR gloves on.

★ This experiment produces toxic and acidic fumes. All heating should be carried out in the fume hood.

★ The precipitate or solution to be discarded during the experiment should be temporarily kept in the tube. After the experiment is completed, it can be collected and poured into the heavy metal waste container.

Step	Procedure	Illustration
2-1	(1) Preparation of a known cation solution: Add 2 drops each of Bi^{3+}, Cu^{2+}, Sb^{3+}, and 8 drops of Sn^{4+} standard solution to a centrifuge tube.	

(2) Check the acidity:
Examine the pH value of the mixed cations solution using universal indicator papers.

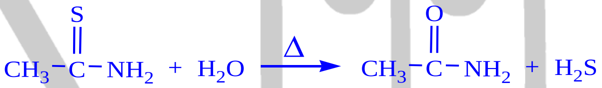
Note 1: To separate group 2 cations from group 3 cations, the pH of the solution should be acidic ($[H^+] = 0.1\sim0.3\ M$) to keep $[S^{2-}]$ low enough, thereby preventing the precipitation of group 3 cations sulfides, which have higher K_{sp} values. However, the pH must not be too low. Since high $[H^+]$ results in low $[S^{2-}]$, 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 the pH value of the solution.

$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq)$

$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq)$

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

Note: Thioacetamide undergoes hydrolysis in aqueous solution to form H_2S.



$$CH_3-\overset{\overset{\displaystyle S}{\|}}{C}-NH_2 + H_2O \xrightarrow{\Delta} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + H_2S$$

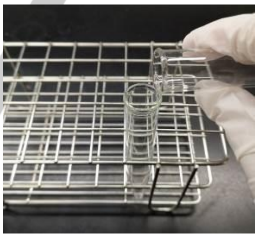
(a)

(b)

(c)

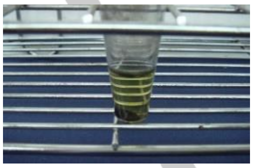
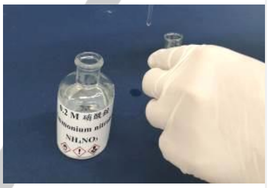
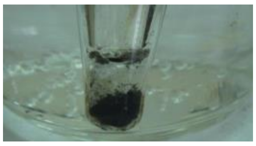
(d)

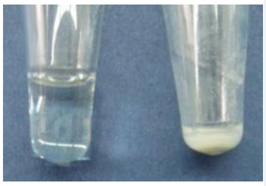
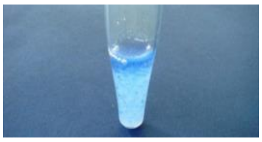
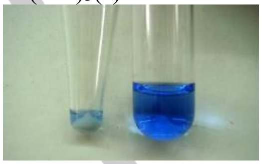
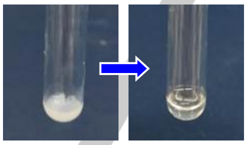
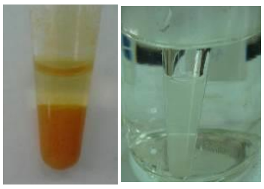
(4) Centrifuge and separation:
Centrifuge and decant the supernatant into another centrifuge tube (soln 2-1). The residue is ppt 2-1. Add 2 more drops of TA to the soln 2-1, and then heat in a warm water bath.

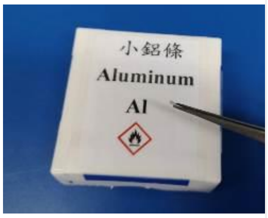


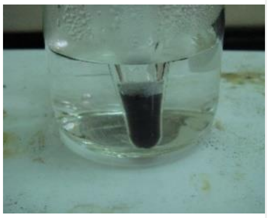
(5) Repeat the precipitation:
Repeat the above precipitation, centrifugation, and separation of the supernatant and ppt several times until no more obvious ppt is formed, indicating that the precipitation of cations is complete.

Note: The precipitation steps are usually conducted two to three times.

2-2	(1) Rinse the precipitate with strong electrolyte: Add 1 drop of 6 *M* NH_4Cl and 20 drops of hot water to the first centrifuge tube to rinse the sulfide ppt. Transfer the mixed solution into the second centrifuge tube to rinse and combine the ppt. After combination and centrifugation, decant the rinsing solution into a test tube. The residue is ppt 2-1; retain it in the centrifuge tube for subsequent analysis. Note: The rinsing solution contains an electrolyte, NH_4Cl, to prevent the formation of colloidal sulfides.	 
	(2) Extraction of Sb_2S_3, SnS_2 with KOH(aq): Add 10 drops of 0.5 *M* KOH to ppt 2-1, mix thoroughly, and heat in a boiling water bath for 5 min.	
	(3) Centrifugation and separation: Centrifuge and decant the supernatant into another centrifuge tube (soln 2-2) and reserve it for the Sn^{4+} and Sb^{3+} test in step 2-6.	
	(4) Repeat the extraction: Repeat the extraction with 10 drops of the KOH(aq). Centrifuge and combine the supernatant with soln 2-2. The residue is ppt 2-2 containing CuS and Bi_2S_3.	
2-3	(1) Rinse the precipitate with strong electrolyte: Rinse the ppt 2-2 with 1 drop of 0.2 *M* NH_4NO_3 and 20 drops of hot water. Centrifuge and decant the rinsing solution to a test tube.	
	(2) Dissolution of CuS and Bi_2S_3: Add 5 drops of DI water and 5 drops of 6 *M* HNO_3 to the ppt 2-2 in the centrifuge tube. Heat in a boiling water bath until the reaction completes. Note: There will be no visible change at the beginning, but bubbling will be observed later, resulting from NO and NO_2 gas produced by the reaction of sulfides and nitric acid. The cloudy, milky-white suspension is due the elemental sulfur. $3\ CuS(s) + 2HNO_3(aq) + 8\ H^+(aq) \rightarrow$ $2\ NO(g) + 3\ S(s) + 3\ Cu^{2+}(aq) + 4\ H_2O(l)$	 CuS, Bi_2S_3  Cu^{2+}, Bi^{3+}, S

	(3) Centrifugation and separation: Centrifuge and transfer the supernatant (soln 2-3) to a clean centrifuge tube to analyze the presence of Cu^{2+} and Bi^{3+}. Keep the residue of elemental sulfur in the tube.	
2-4	(1) Separation of Cu^{2+} from Bi^{3+}: Add conc. ammonia water to soln 2-3 until it is basic. Note: Check with a litmus paper.	 
	(2) Identification of Cu^{2+}: Centrifuge and decant the supernatant into a test tube (soln 2-4), and the small amount of white residue is ppt 2-4. The presence of Cu^{2+} in soln 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.	
2-5	(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. $SnCl_2 \xrightarrow{NaOH(aq)} Sn(OH)_2(s) \xrightarrow{NaOH(aq)} [Sn(OH)_3]^-(aq)$	
	(2) Identification of Bi^{3+}: Add freshly prepared sodium stannite reagent to precipitate 2-4. The presence of Bi^{3+} is indicated by the immediate formation of Bi metal (black deposit). $2\ Bi(OH)_3(s) + 3\ [Sn(OH)_3]^-(aq) + 3OH^-(aq)$ $\rightarrow\ 2\ Bi(s) + 3\ [Sn(OH)_6]^{2-}(aq)$	
2-6	(1) Production of $[SnCl_6]^{2-}$ and $[SbCl_4]^-$: Add conc. hydrochloric acid to soln 2-2 drop by drop. Stir and mix the solution to observe the formation of $Sb_2S_3(s)$ and $SnS_2(s)$, then subsequent dissolution for forming complex ions, $[SnCl_6]^{2-}$ and $[SbCl_4]^-$. Heat in a hot water bath to complete the reaction.	

	(2) Centrifugation and separation: Centrifuge and pour the supernatant (soln 2-5) into an evaporating dish. Keep the residue in the tube. Note: The evaporating dish and crucible tongs should be cleaned first.	
2-7	(1) Evaporation of excess acid: In the fume hood, place evaporating dish on a hot plate to evaporate soln 2-5 slowly to *ca.* 4 drops remain. Note: If evaporation is carried too far, some $SnCl_4$ may be lost.	
	(2) Dilution with DI water: 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, separately.	
2-8	**Sb test (test tube)** Add 1/4 spatula of solid $H_2C_2O_4$ and 2 drops of TA to the solution. Warm it in the hot water bath. The formation of an orange $Sb_2S_3(s)$ confirms the presence of Sb^{3+}. Note: $C_2O_4^{2-}$ and Sn^{4+} form a stable $[Sn(C_2O_4)_3]^{2-}$ complex, so it will not obscure the formation and color of the Sb_2S_3 precipitate. $2\,[SbCl_4]^-(aq) + 3\,H_2S(aq) \rightarrow$ $Sb_2S_3(s) + 6\,H^+(aq) + 8\,Cl^-(aq)$	 
2-9	**Sn test (centrifuge tube)** (1) Add a small aluminum strip (5 mm) and 10 drops of 6 *M* HCl to the solution. Heat in the hot water bath to dissolve the aluminum. Note: Aluminum can reduce Sn^{4+} and Sb^{3+} to Sn^{2+} and Sb, respectively, in an acidic solution. $[SbCl_4]^-(aq) + Al(s) \rightarrow Sb(s) + Al^{3+}(aq) + 4\,Cl^-(aq)$ $[SnCl_6]^{2-}(aq) + Al(s) + H^+(aq)$ $\rightarrow Sn^{2+}(aq) + H_2(g) + Al^{3+}(aq)$ (unbalanced)	 

	(2) Centrifugation and separation: Centrifuge, and decant the supernatant to another test tube. Note: A black precipitate may indicate the presence of Sb^{3+}.	
	(3) Identification of Sn^{4+}: Add 2 drops of $HgCl_2(aq)$ to the solution. The formation of a white-to-gray precipitate (Hg_2Cl_2 and Hg) indicates the presence of Sn^{2+}. Note: Since Sn^{2+} will be oxidized by O_2, the $HgCl_2(aq)$ should be added as soon as possible. $Sn^{2+}(aq) + 2\ HgCl_2(aq)$ $\rightarrow Hg_2Cl_2(s) + Hg(l) + Sn^{4+}(aq)$ (unbalanced)	
2-10	(1) Keep and present the identification products to the lab instructor when finishing the experiment.	
	(2) The liquid waste containing heavy metals should be collected and discarded into the recycling container. Brush all glassware and remove labels from test tubes and centrifuge tubes.	

References

1. King, E. J. *Qualitative Analysis and Electrolytic Solutions*; Harcourt, Brace: New York, 1976.