

Experiment 3

QUALITATIVE ANALYSIS OF GROUP 1 CATIONS

Objective

The purpose of this experiment is to learn the techniques to separate and identify some common cations, and to understand the principles for the equilibria of precipitation and complex formation.

Lab techniques

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

Introduction

Analysis of the identity and quantity of metallic elements in compounds or samples is an integral part of chemical research. Before the advent of modern analytical instruments (such as the atomic absorption spectrophotometer), metallic cations were analyzed and identified with a simple method involving the use of common reagents and basic instruments, as well as the application of the equilibrium concepts of precipitation, dissolution, and complex formation. The application of qualitative analysis of cations covers a very wide range of fields, including environmental or soil analysis and materials research. In this experiment, students will learn basic principles and procedures for separating and identifying cations.

Qualitative analysis of cations usually consists of three stages. First, based on the different solubility properties, the cations are separated into 5 groups through the successive addition of selective precipitating reagents. Second, within each group, precipitated cations are separated through selective dissolution processes. Last, the presence of each cation is verified through different identification tests. The cations are classified into the following 5 groups:

I. Systematic analysis of cations into five groups

Group 1 cations (Hg_2^{2+} , Ag^+ , and Pb^{2+} ; insoluble chlorides):

Among the common metallic cations, only these three cations can form insoluble chlorides with hydrochloric acid. When 6 M HCl is added to the solution, white precipitates of Hg_2Cl_2 , AgCl , and PbCl_2 are formed. Other metallic cations remain in solution.

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

After the insoluble chlorides are isolated, the pH of the solution is adjusted to 0.5, and then $\text{H}_2\text{S}(\text{aq})$ is added. Since the concentration of sulfide ion (S^{2-}) is very low at low pH, only those metallic sulfides having very low K_{sp} values, *i.e.* HgS , PbS , CuS , Bi_2S_3 , CdS , As_2S_3 , Sb_2S_3 , and SnS_2 , will precipitate. Cations with larger K_{sp} values of their sulfides, such as Zn^{2+} and Ni^{2+} , remain in the solution.

Group 3 cations (Al^{3+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cr^{3+} , Zn^{2+} , and Mn^{2+} ; insoluble sulfides or hydroxides in alkaline solution):

After isolating the insoluble sulfides in an acidic medium, the solution is made basic, and then $\text{H}_2\text{S}(\text{aq})$ is added. In an alkaline solution, the concentration of S^{2-} increases, and the metallic sulfides with larger K_{sp} values, such as ZnS , NiS , CoS , and MnS , precipitate. Moreover, since the solution is basic, Al^{3+} , Fe^{3+} , and Cr^{3+} form insoluble hydroxides and are also separated from the solution.

Group 4 cations (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} ; carbonate precipitates):

These four metallic cations all belong to Group IIA in the periodic table, and therefore their chemical properties are very similar. They form soluble chlorides and sulfides and hence are separable from group 1, 2, and 3 cations. However, their carbonates precipitate in a mixture of $(\text{NH}_4)_2\text{CO}_3/\text{NH}_4\text{Cl}/\text{NH}_3$ solution.

Group 5 cations (Na^+ , K^+ , and NH_4^+ ; soluble cations):

None of the cations in this group form precipitates in the separation processes of group 1~4 cations and thus remain in the final solution.

The flow chart 3-1 shows the separation of these cations into 5 groups. The systematic analysis of group 1 cations (flow chart 3-2) will be practiced in this experiment as the following.

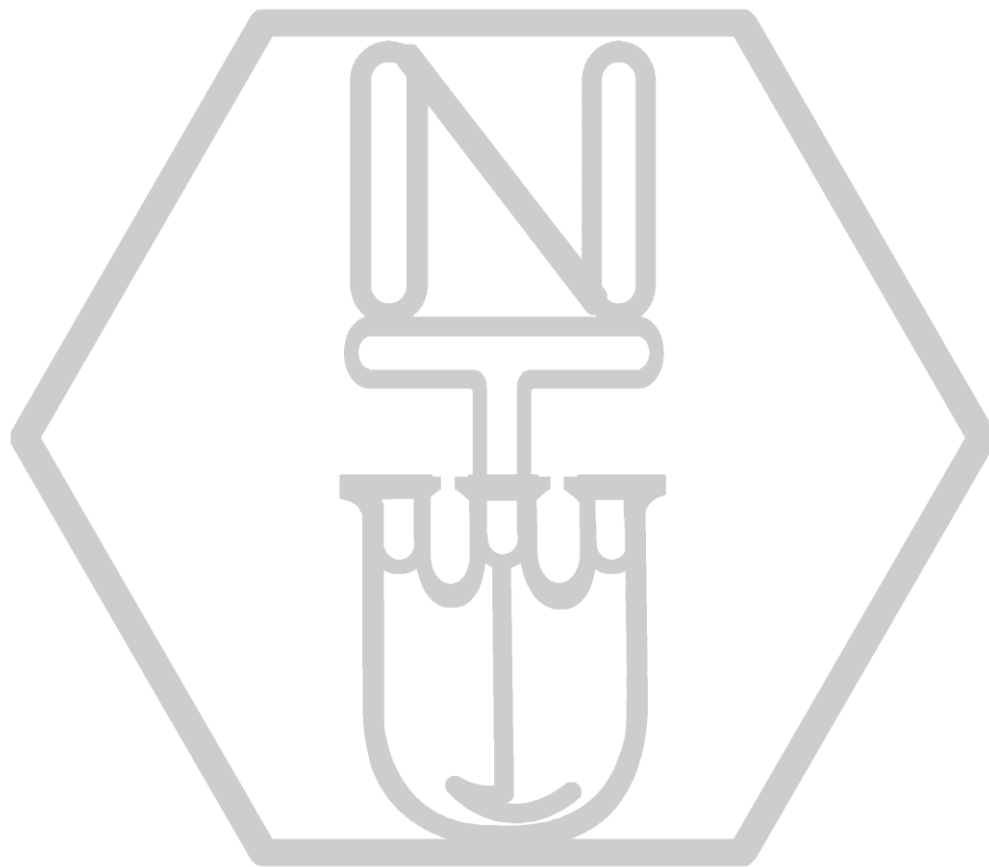
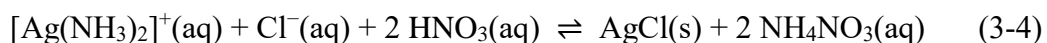
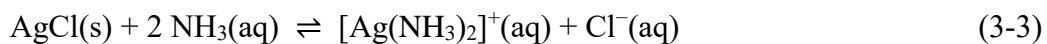
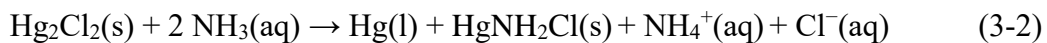
II. Systematic separation of group 1 cations

Among the common cations, only Hg_2^{2+} , Ag^+ , and Pb^{2+} may form insoluble chlorides with hydrochloric acid and precipitate out. The solubility of PbCl_2 increases with increasing temperature. Therefore, hot water may extract and separate PbCl_2 from solid Hg_2Cl_2 and AgCl . The Pb^{2+} ions dissolved in hot water can further react with the added $\text{K}_2\text{CrO}_4(\text{aq})$ to produce a yellow precipitate, indicating its presence, as shown in equation 3-1.

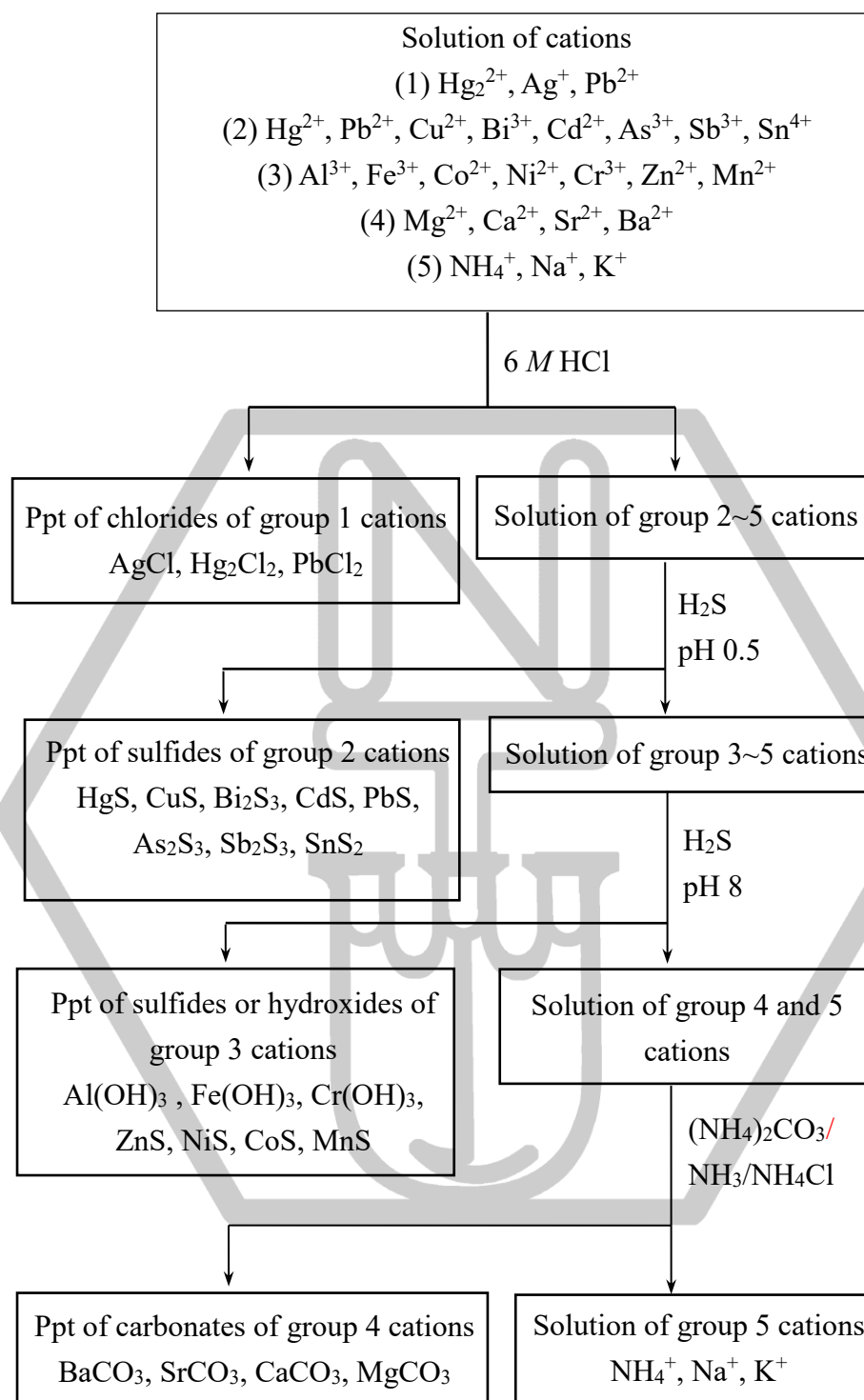


Concentrated ammonia water is then added to the residue containing Hg_2Cl_2 and AgCl precipitates. Hg_2Cl_2 undergoes a disproportionation reaction to form a black mixed precipitate of $\text{HgNH}_2\text{Cl}(\text{s})$ and $\text{Hg}(\text{l})$, indicating the presence of Hg_2^{2+} , as shown

in equation 3-2. On the other hand, AgCl reacts with ammonia water to form $[\text{Ag}(\text{NH}_3)_2]^+$ complex ion that dissolves, as shown in equation 3-3. After adding enough nitric acid to the solution containing these complex ions to acidify the solution, white AgCl precipitates will appear again, indicating the presence of Ag^+ , as shown in equation 3-4. The Pb^{2+} , Hg_2^{2+} , and Ag^+ cations are thus separated and identified in sequence.



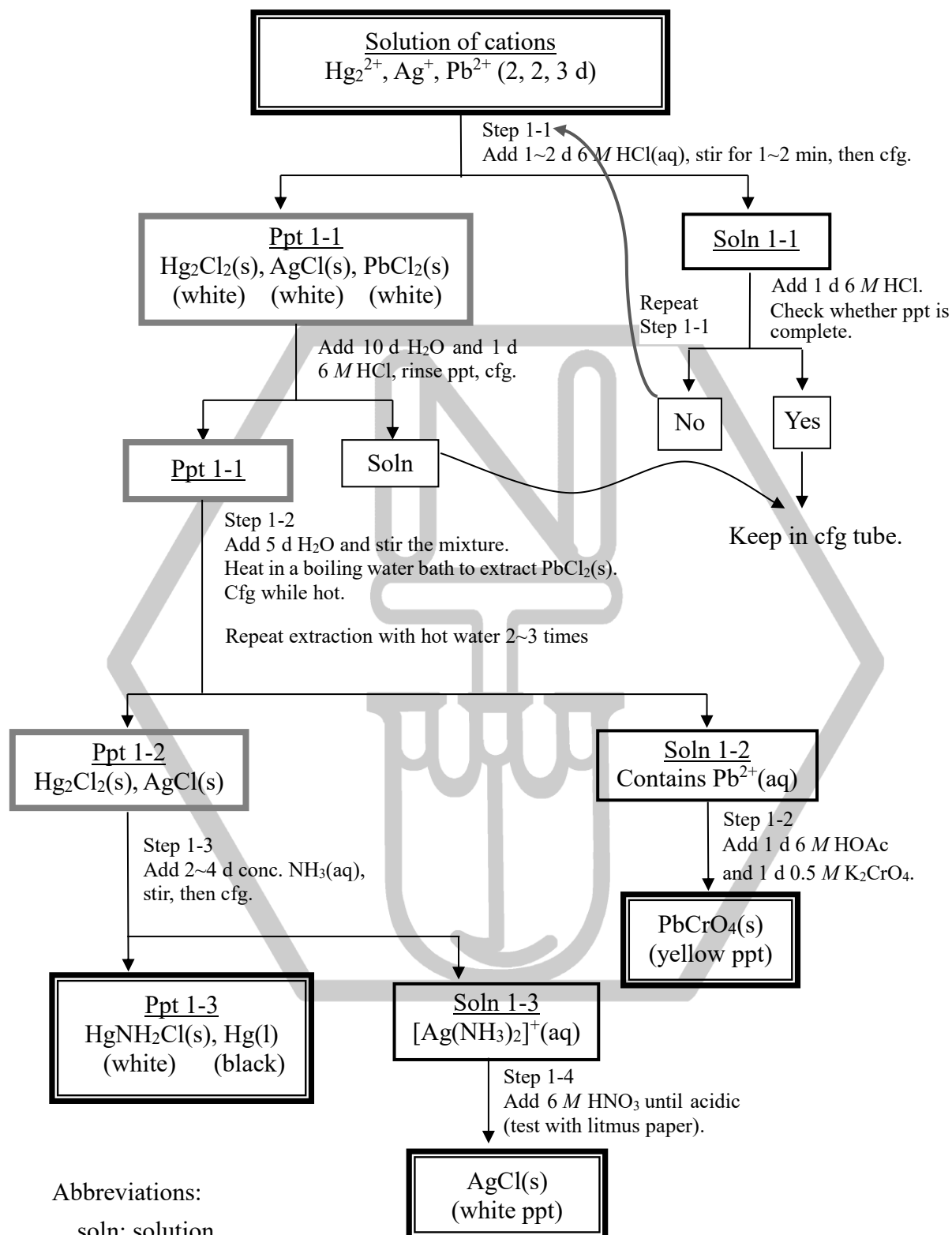
Flow chart 3-1: Systematic separation of cations into five groups



Abbreviations:

ppt: precipitate; precipitation

Flow chart 3-2: Separation and identification of group 1 cations



Abbreviations:

soln: solution

d: drop; drops

conc.: concentrated

cfg: centrifuge; centrifugation

DI water: deionized water

Apparatus

Centrifuge, centrifuge tube (5), glass rod, test tube (10), test tube holder, test tube rack, dropper, NBR gloves, and litmus paper.

Shared: stirrer/hot plate, beaker (400 mL), and vortex mixer.

Chemicals

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

Hg_2^{2+} : mercury(I) nitrate dihydrate, $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$

Ag^+ : silver nitrate, AgNO_3

Pb^{2+} : lead(II) nitrate, $\text{Pb}(\text{NO}_3)_2$

II. Test reagents:

6 M Hydrochloric acid, $\text{HCl}(\text{aq})$

0.5 M Potassium chromate, K_2CrO_4



6 M Acetic acid, CH_3COOH

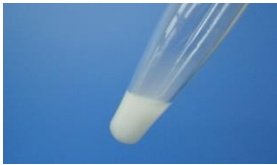

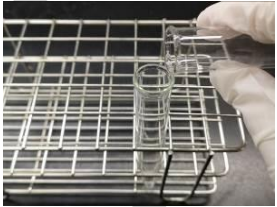


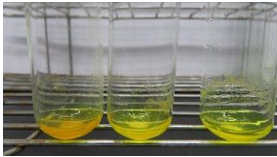
6 M Nitric acid, HNO_3


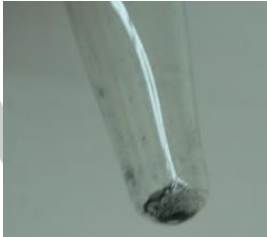

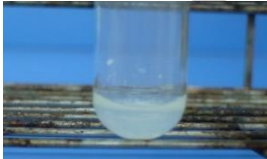
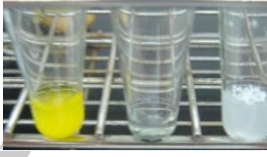

Concentrated ammonia water, 15 M $\text{NH}_3(\text{aq})$

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
1-1	(1) Preparation of a known cation solution: Add 2, 2, and 3 drops of the standard Hg_2^{2+} , Ag^+ , and Pb^{2+} solutions, respectively, to one centrifuge tube.	
	(2) Precipitation of chlorides: Add 1 drop of 6 M HCl to the centrifuge tube. Stir for 1~2 min. If precipitation is observed, wait until the precipitate settles and add another drop of 6 M HCl. Examine whether more white precipitate is produced. If a new precipitate is formed, keep adding 6 M HCl drop by drop until no further precipitation is observed.	

	<p>Note 1: PbCl_2 precipitates relatively slowly. Stir 1~2 min can help PbCl_2 precipitate completely.</p> <p>Note 2: Do not add excess hydrochloric acid, otherwise it may dissolve the chlorides. 2~3 drops are typically enough.</p>	
	<p>(3) Centrifugation and separation:</p> <p>Centrifuge and decant the supernatant into another centrifuge tube (soln 1-1). The residue is ppt 1-1. Add one drop of hydrochloric acid to soln 1-1 to check whether the precipitation is complete. If not, repeat step 1-1-2 until no new precipitate forms.</p>	
	<p>(4) Rinse the chlorides:</p> <p>Add 10 drops of DI water and 1 drop of 6 M HCl to rinse ppt 1-1. Centrifuge and discard the supernatant in a test tube. Keep the residue in the cfr. tube (ppt 1-1) for the following analysis.</p>	
1-2	<p>(1) Extraction of PbCl_2:</p> <p>Add 5 drops of DI water to ppt 1-1 and stir the mixture. Place the tube in a boiling water bath for several min. Centrifuge the hot solution as soon as possible, and transfer the supernatant (soln 1-2) into another centrifuge tube.</p> <p>Note: If there is a delay before centrifugation, the solution cools down, $\text{PbCl}_2(\text{s})$ may precipitate again.</p>	
	<p>(2) Identification of Pb^{2+}:</p> <p>Add 1 drop of 6 M CH_3COOH and 1 drop of 0.5 M K_2CrO_4 to soln 1-2. A yellow PbCrO_4 ($K_{\text{sp}} = 2.8 \times 10^{-13}$) precipitate indicates the presence of Pb^{2+}.</p> <p>Note: The addition of CH_3COOH prevents the precipitation of other chromates, such as CuCrO_4 ($K_{\text{sp}} = 3.6 \times 10^{-6}$).</p>	
	<p>(3) Repeat extraction:</p> <p>Extract ppt 1-1 with hot water followed by centrifugation (step 1-2) 2~3 times until the decanted supernatant is only slightly turbid when K_2CrO_4 is added. The remaining solid is ppt 1-2.</p>	

	Note: If Pb^{2+} is not completely removed, it will affect the results of subsequent tests.	
1-3	<p>(1) Separation of Hg_2Cl_2 and AgCl: Add 2~4 drops of conc. ammonia water to ppt 1-2. Disperse the precipitate with a glass rod or vortex mixer.</p>	
	<p>(2) Identification of Hg_2^{2+}: Centrifuge, transfer the supernatant (soln 1-3) into a clean test tube, and examine the color of the residue (ppt 1-3). Black residue indicates the presence of Hg(l) and $\text{HgNH}_2\text{Cl(s)}$ mixture.</p> <p>Note: If ppt 1-2 is not Pb-free, it produces white $\text{Pb(OH)}_2\text{(s)}$ precipitate after adding conc. ammonia water.</p>	 $\text{HgNH}_2\text{Cl(s)} + \text{Hg(l)}$
1-4	<p>Identification of Ag^+: Acidify soln 1-3 by adding 6 M HNO_3. Observe any change that occurs. A white precipitate proves the presence of Ag^+.</p> <p>Note: Mix the solution thoroughly after adding the acid. Use a glass rod to spot the solution on a piece of litmus paper to test the acidity.</p>	 
1-5	<p>(1) Keep and present the identification products to the lab instructor when finishing the experiment.</p>	
	<p>(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.</p> <p>(3) Wash the apparatus, clean up your benchtop, and complete the experiment.</p>	

References

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