EXPERIMENT 13
QUALITATIVE ANALYSIS

PURPOSE:

1. To separate and identify each cation in a mixture of **Ag^+, Cu^{2+}, Zn^{2+}**, and **Ca^{2+}** cations.
2. To identify the cations present in three individually assigned unknown mixtures that may contain any or all of the above listed cations.

PRINCIPLES:

Qualitative analysis involves the identification of the substances in a mixture. When chemical methods are used in the identification of mixtures of metal cations, these ions are usually separated before identification can occur. After they have been separated, identification of each cation depends on the observation of a characteristic chemical reaction. Solubility equilibrium and complex-ion equilibrium play crucial roles in the separations and subsequent identifications.
You will be working with mixtures of **Ag^+, Cu^{2+}, Zn^{2+}, and Ca^{2+}** ions. These cations belong to Analytical Groups I, II, III, and IV. Before you do the experiment, spend some time studying the scheme and reading the following description.

Hydrochloric acid will be used to precipitate Ag^+ as a white precipitate of AgCl. If you do not observe a precipitate with your unknown mixture, this cation cannot be present. The formation of a precipitate, however, is not considered sufficient evidence for the presence of Ag^+ in either a known or an unknown mixture. As a confirmatory test for this cation, this precipitate should dissolve in aqueous ammonia with the formation of a complex ion and should reappear when the solution is treated with an acid.
Hydrogen sulfide is required for the next two separations. A saturated solution (0.10 *M)* of this substance will be generated by heating a solution of thioacetamide, CH_3CSNH_2. Hydrolysis (reaction with water) has the following result:

$$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$$

This reagent will be used to precipitate **Cu^{2+}** as black **CuS** precipitate from a 0.3 *M* H_3O^+ solution and to precipitate **Zn^{2+}** as white/pale yellow **ZnS** precipitate from a weakly basic solution. Another problem will show that both CuS and ZnS will precipitate from a weakly basic solution but that only CuS will precipitate from a 0.3 *M* H_3O^+ solution. Therefore, separation of these ions will occur only if precipitation is achieved first under acidic conditions and then under basic conditions. If a precipitate does not form in the acidic solution of your unknown mixture, Cu^{2+} must be absent. Similarly, Zn^{2+} cannot be in your unknown mixture if a precipitate is not formed in the weakly basic solution.

You will then dissolve each of these metal sulfides in nitric acid. This reagent will oxidize the sulfide ion to elemental sulfur. The solution should be blue for $Cu^{2+}(aq)$ and colorless for $Zn^{2+}(aq)$. The confirmatory test for each cation involves the addition of potassium ferrocyanide, $K_4Fe(CN)_6$, to these solutions. A red-maroon precipitate confirms the presence of Cu^{2+}, whereas a white precipitate confirms the presence of Zn^{2+}. You should note that $Fe(CN)_6^{4-}$ is a complex ion that is considerably less toxic and dangerous than the cyanide ion, CN^-.

Finally Ca^{2+} will be precipitated as white $CaCO_3$ by the addition of $(NH_4)_2CO_3$. This precipitate will dissolve in an acid with the evolution of carbon dioxide. If a precipitate does not form, Ca^{2+} cannot be present in your unknown mixture. The confirmatory test for this cation involves the precipitation of the white oxalate, CaC_2O_4, upon the addition of $K_2C_2O_4$.

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PROCEDURE:

A. PRELIMINARY PREPARATIONS.

1. Instructions for using the test tubes:

- Obtain 6 small test tubes.
- Set up a boiling water bath in a fume hood using a beaker of water placed on a heating plate.
- Measure 1 mL of D.I water in a test tube and use the level of water in this test tube to match subsequent volume measurements of 1mL.
- Measure 1 mL of D.I water in a test tube and use the level of water in this test tube to match
- Use labeled test tubes throughout the experiment so that you do not confuse the solutions and the precipitates at any time.

2. Instructions for using the centrifuges:

- Never fill the centrifuge tubes to a height more than 1 cm from the top.
- Label the test (centrifuge) tubes to avoid confusion.
- **Balance the centrifuge**:
  Always operate with an even number of test (centrifuge) tubes, containing equal volumes of liquid, placed opposite one another; this balances the centrifuge and eliminates excessive vibration and wear.
- If only one tube needs to be centrifuged, balance it with a tube containing the same volume of solvent.
- When you use a centrifuge, do not attempt to stop the centrifuge rotor with your finger or anything else.

3. Handling the solutions used in this experiment:

- Thioacetamide is a carcinogen. Avoid contact with your skin.In addition to having a foul odor, the hydrogen sulfide generated during the hydrolysis of thioacetamide is extremely toxic. Although only small amounts of H_2S usually escape from the solution, work under a hood whenever possible.
- Hydrochloric acid, ammonia, nitric acid, and acetic acid can cause chemical burns in addition to ruining your clothes. If you spill any of these solutions on you, wash the contaminated area thoroughly with tap water and report the incident to your instructor. You may require further treatment.
- Wash your hands thoroughly after using oxalate solutions since they are poisonous.
- Obtain instructions for discarding the solutions that you will use in this experiment.

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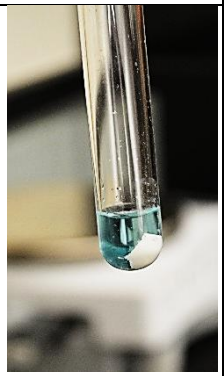
B. DOING THE ANALYSIS

PART I: Analysis of the known mixture

Obtain 1 mL of the known mixture in a small test tube. This solution contains:

$AgNO_3$ 0.1 M
$Cu(NO_3)_2$ 0.2 M
$Zn(NO_3)_2$ 0.2 M
$Ca(NO_3)_2$ 0.2 M

1. Separation of Ag^+ from Cu^{2+}, Zn^{2+} and Ca^{2+} and Identification of Ag^+ in the Known Mixture

Separation of Ag^+ from Cu^{2+}, Zn^{2+} and Ca^{2+}	**Confirmatory Test for Ag^+**
Add 2 drops of 6 M HC1. A white precipitate of AgCl will form. Stir the mixture with a clean stirring rod. Centrifuge the mixture for about 1 min. 	Add 10 drops of 6 M NH_3 to the precipitate. If necessary, stir the mixture with a clean stirring rod until the precipitate dissolves.
Check for complete precipitation by adding 1 more drop of 6 M HCl. Avoid using excess HCl. If a precipitate has formed, centrifuge the mixture and check again for complete precipitation. Continue this process until no precipitate is formed.	Add 6 *M* HNO_3 by drops until a white precipitate appears. This reaction confirms the presence of Ag^+. 
Decant (pour off) the solution into a clean test tube. Save this solution for Step 2. Use the precipitate to confirm the presence of Ag^+ by performing the confirmatory test for Ag^+ (See right hand side column)	

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2. Separation of Cu^{2+} from Zn^{2+} and Ca^{2+} and Identification of Cu^{2+} in the Known Mixture

Separation of Cu^{2+} from Zn^{2+} and Ca^{2+}	**Confirmatory Test for Cu^{2+}**
Add 6 M NH_3 by drops to the solution from Step 1 until a drop of the solution on a clean stirring rod causes pink litmus paper to turn blue.	Wash the black CuS precipitate by stirring it vigorously with 1 mL of distilled water. Use a clean stirring rod. Centrifuge the mixture, save the precipitate, and discard the water.
Estimate the volume of the solution to the nearest 0.5 mL. Make the estimate by comparing the volume with measured amounts in a similar test tube. Mentally, add 0.6 mL to that volume to account for the dilution that will occur in the next steps. Round the result to the nearest milliliter. Add 1 drop of 6 M HC1 to the solution for every milliliter that results from this procedure. The concentration of H_3O^+ in the solution will be 0.3 M after the dilution in the next step is completed.	Add 20 drops of 6 M $HN0_3$ to the precipitate. Place the test tube in the boiling water bath for several minutes. Stir occasionally with a clean stirring rod. Separate any sulfur or traces of undissolved sulfides by centrifuging. Discard the solid undissolved residue and use the solution in the next step.
Add 12 drops of 1 M thioacetamide to the solution. Place the test tube in the boiling water bath for about 10 minutes. A black precipitate of **CuS** will form. 	Add drops of 6 M NH_3 carefully until the solution turns pink litmus paper blue. Then add drops of 6 *M* acetic acid until the solution turns blue litmus paper pink.
Centrifuge the mixture and decant the clear solution into a clean test tube. Save the black **CuS** precipitate to confirm the presence Cu^{2+} by performing the **confirmatory test for Cu^{2+}.** (See right hand side column). 	Add 10 drops of 0.1 M $K_4Fe(CN)_6$ and mix thoroughly. A red-maroon precipitate confirms the presence of Cu^{2+}. 
Test the solution for complete precipitation by adding 3 more drops of 1M thioacetamide and reheating for 5 min. If no precipitate forms, save the solution for Step 3. If a precipitate forms, centrifuge the mixture, save the solution for Step 4, and discard the precipitate.	

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3. Separation of Zn^{2+} from Ca^{2+} and Identification of Zn^{2+} in the Known Mixture

Separation of Zn^{2+} from Ca^{2+}	Confirmatory Test for Zn^{2+}
Estimate the volume of the solution from Step 3 by comparing it with 3 mL of water in a similar test tube. If the volume is 3 mL or less, proceed to the next step. If it is greater than 3 mL, place the solution in the boiling water bath until that volume is attained.	Wash the white/pale yellow ZnS precipitate by stirring it vigorously with 2 mL of distilled water to which you have added 1 drop of 6 M NH_3. Use a clean stirring rod. Centrifuge the mixture, save the precipitate, and discard the water.
Add 10 drops of 6 M HC1 followed by 10 drops of 6 M NH_3. Then add drops of 6 M NH_3 until the solution is basic to litmus paper. Add 5 more drops of 6 M NH_3.	Add 20 drops of 6 M $HN0_3$ to the precipitate. Place the test tube in the boiling water bath for several minutes. Stir occasionally with a clean stirring rod. Separate any sulfur or traces of undissolved sulfides by centrifuging. Discard the residue and use the solution in the next step.
Add 12 drops of 1M thioacetamide. Stir thoroughly and heat for 10 min in the boiling water bath. A white/pale yellow ZnS precipitate will form. 	Add drops of 6 M NH_3 carefully until the solution turns pink litmus paper blue. Then add drops of 6 *M* acetic acid until the solution turns blue litmus paper pink.
Centrifuge the mixture and decant the clear solution into a clean test tube. Save this solution for Step 4. Save the white/pale yellow precipitate to confirm the presence of Zn^{2+}, by performing the **confirmatory test for Zn^{2+}** (See right hand side column).	Add 10 drops of 0.1 M $K_4Fe(CN)_6$ and mix thoroughly. A white precipitate confirms the presence of Zn^{2+}.

4. Separation and Identification of Ca^{2+} in the Known Mixture

Separation of Ca^{2+}	Confirmatory Test for Ca^{2+}
Add 10 drops of 3 M $(NH_4)_2CO_3$ to the solution from Step 3. A white precipitate of $CaCO_3$ will form.	Wash the precipitate by stirring it vigorously with 1 mL of distilled water. Use a clean stirring rod. Centrifuge the mixture, save the precipitate, and discard the water.
Centrifuge the mixture, discard the solution and save the white $CaCO_3$ precipitate to confirm the presence of Cu^{2+} by performing the **confirmatory test for Cu^{2+}.** (See right hand side column).	Dissolve the precipitate by adding 5 drops of 6 *M* acetic acid.
	Make the solution basic to litmus paper using 6 *M* NH_3.
	Add 10 drops of 1 *M* $K_2C_2O_4$. A white precipitate of CaC_2O_4 that should form within a few minutes confirms the presence of Ca^{2+}.

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PART II: Analysis of the unknown mixtures

The general procedure for the separation and confirmation of the cations outlined for the known mixture will be followed with several modifications, depending on the composition of the unknowns assigned to you.

Be aware, that in the analysis of an unknown mixture, carrying out a careful confirmatory test for the presence of a cation you suspect to be present is crucial for the correct identification of the cation.

Obtain 1 mL of one unknown mixture in a small test tube. Recall that this solution may contain any or all of the four cations (**Ag^+, Cu^{2+}, Zn^{2+} and Ca^{2+}**)

1. Separation of Ag^+ from Cu^{2+}, Zn^{2+} and Ca^{2+} and Identification of Ag^+ in the Unknown Mixture

Separation of Ag^+ from Cu^{2+}, Zn^{2+} and Ca^{2+}	**Confirmatory Test for Ag^+**
Add 2 drops of 6 M HC1. If no precipitate forms, proceed to Step 2. If a white precipitate of AgCl forms, stir the mixture with a clean stirring rod. Centrifuge the mixture for about 1 min.	Add 10 drops of 6 M NH_3 to the precipitate. If necessary, stir the mixture with a clean stirring rod until the precipitate dissolves.
Check for complete precipitation by adding 1 more drop of 6 M HCl. Avoid using excess HCl. If a precipitate has formed, centrifuge the mixture and check again for complete precipitation. Continue this process until no precipitate is formed.	Add 6 *M* HNO_3 by drops until a white precipitate appears. These reactions confirm the presence of Ag^+.
Decant (pour off) the solution into a clean test tube. Save this solution for Step 2. Use the precipitate to confirm the presence of Ag^+ by performing the confirmatory test for Ag^+ (See right hand side column)	

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2. Separation of Cu^{2+} from Zn^{2+} and Ca^{2+} and Identification of Cu^{2+} in the Unknown Mixture

Separation of Cu^{2+} from Zn^{2+} and Ca^{2+}	**Confirmatory Test for Cu^{2+}**
Add 6 M NH_3 by drops to the solution from Step 1 until a drop of the solution on a clean stirring rod causes pink litmus paper to turn blue.	Wash the black CuS precipitate by stirring it vigorously with 1 mL of distilled water. Use a clean stirring rod. Centrifuge the mixture, save the precipitate, and discard the water.
Estimate the volume of the solution to the nearest 0.5 mL. Make the estimate by comparing the volume with measured amounts in a similar test tube. Mentally, add 0.6 mL to that volume to account for the dilution that will occur in the next steps. Round the result to the nearest milliliter. Add 1 drop of 6 M HC1 to the solution for every milliliter that results from this procedure. The concentration of H_3O^+ in the solution will be 0.3 M after the dilution in the next step is completed.	Add 20 drops of 6 M $HN0_3$ to the precipitate. Place the test tube in the boiling water bath for several minutes. Stir occasionally with a clean stirring rod. Separate any sulfur or traces of undissolved sulfides by centrifuging. Discard the residue and use the solution in the next step.
Add 12 drops of 1 M thioacetamide to the solution. Place the test tube in the boiling water bath for about 10 minutes. If no precipitate forms during this time, proceed to Step 3. If a black precipitate of **CuS** forms, proceed with the step that follows below.	Add drops of 6 M NH_3 carefully until the solution turns pink litmus paper blue. Then add drops of 6 *M* acetic acid until the solution turns blue litmus paper pink.
Centrifuge the mixture and decant the clear solution into a clean test tube. Save the black **CuS** precipitate to confirm the presence of Cu^{2+} by performing the **confirmatory test for Cu^{2+}.** (See right hand side column).	Add 10 drops of 0.1 M $K_4Fe(CN)_6$ and mix thoroughly. A red-maroon precipitate confirms the presence of Cu^{2+}.
Test the solution for complete precipitation by adding 3 more drops of 1M thioacetamide and reheating for 5 min. If no precipitate forms, save the solution for Step 3. If a precipitate forms, centrifuge the mixture, save the solution for Step 3, and discard the precipitate.	

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3. Separation of Zn^{2+} from Ca^{2+} and Identification of Zn^{2+} in the Unknown Mixture

Separation of Zn^{2+} from Ca^{2+}	Confirmatory Test for Zn^{2+}
Estimate the volume of the solution from Step 3 by comparing it with 3 mL of water in a similar test tube. If the volume is 3 mL or less, proceed to the next step. If it is greater than 3 mL, place the solution in the boiling water bath until that volume is attained.	Wash the white/pale yellow ZnS precipitate by stirring it vigorously with 2 mL of distilled water to which you have added 1 drop of 6 M NH_3. Use a clean stirring rod. Centrifuge the mixture, save the precipitate, and discard the water.
Add 10 drops of 6 M HC1 followed by 10 drops of 6 M NH_3. Then add drops of 6 M NH_3 until the solution is basic to litmus paper. Add 5 more drops of 6 M NH_3.	Add 20 drops of 6 M $HN0_3$ to the precipitate. Place the test tube in the boiling water bath for several minutes. Stir occasionally with a clean stirring rod. Separate any sulfur or traces of undissolved sulfides by centrifuging. Discard the residue and use the solution in the next step.
Add 12 drops of 1M thioacetamide. Stir thoroughly and heat for 10 min in the boiling water bath. If no precipitate forms during this time, proceed to Step 4. If a white/pale yellow ZnS precipitate forms proceed with the step that follows below.	Add drops of 6 M NH_3 carefully until the solution turns pink litmus paper blue. Then add drops of 6 *M* acetic acid until the solution turns blue litmus paper pink.
Centrifuge the mixture and decant the clear solution into a clean test tube. Save this solution for Step 4. Save the white/pale yellow precipitate to confirm the presence of Zn^{2+} , by performing the **confirmatory test for Zn^{2+}** (See right hand side column).	Add 10 drops of 0.1 M $K_4Fe(CN)_6$ and mix thoroughly. A white precipitate confirms the presence of Zn^{2+}.

4. Separation and Identification of Ca^{2+} in the Unknown Mixture

Separation of Ca^{2+}	Confirmatory Test for Ca^{2+}
Add 10 drops of 3 M $(NH_4)_2CO_3$ to the solution from Step 3. If no precipitate forms, you have completed the analysis. If a white precipitate of $CaCO_3$ forms proceed with the step that follows below.	Wash the precipitate by stirring it vigorously with 1 mL of distilled water. Use a clean stirring rod. Centrifuge the mixture, save the precipitate, and discard the water.
Centrifuge the mixture, discard the solution and save the white $CaCO_3$ precipitate to confirm the presence of Ca^{2+} by performing the **confirmatory test for Ca^{2+}.** (See right hand side column).	Dissolve the precipitate by adding 5 drops of 6 *M* acetic acid.
	Make the solution basic to litmus paper using 6 *M* NH_3.
	Add 10 drops of 1 *M* $K_2C_2O_4$. A white precipitate of CaC_2O_4 that should form within a few minutes confirms the presence of Ca^{2+}.

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REPORT FORM

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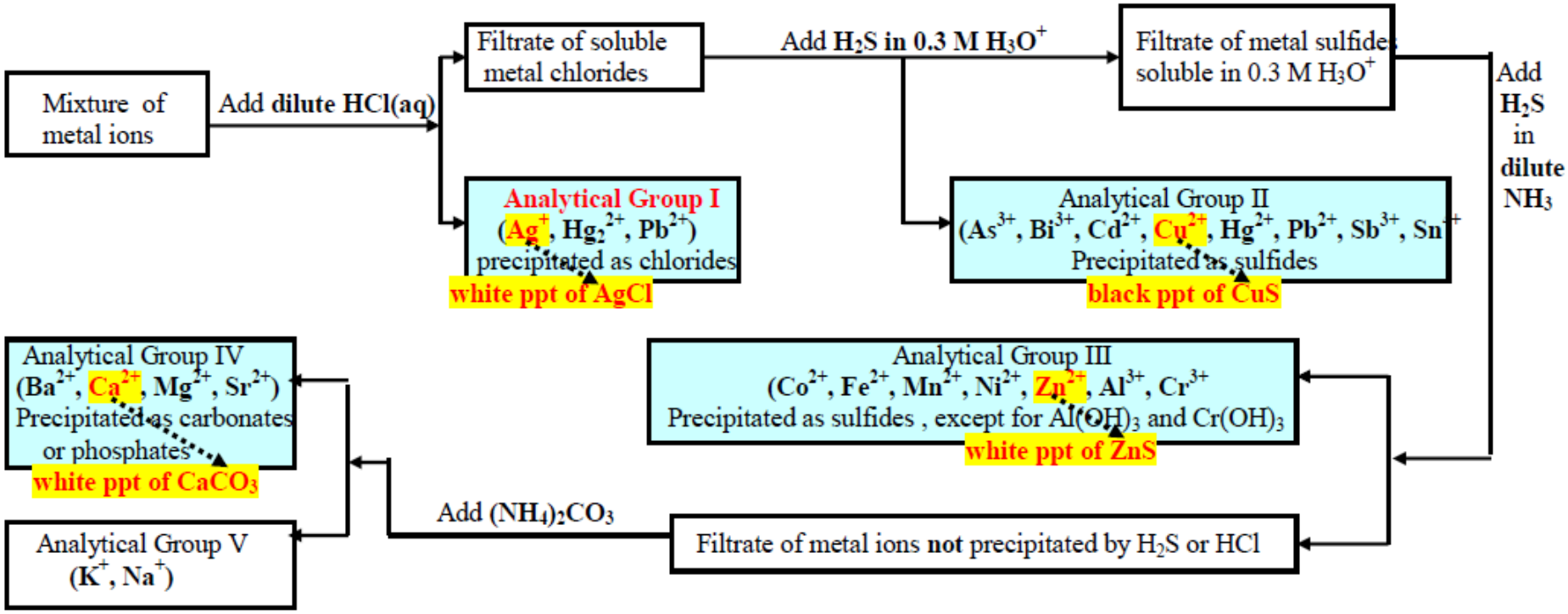

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