Experiment 7: Qualitative Analysis of Cations

Purpose: Develop a systematic scheme of separation and analysis of a selected group of cations.

Introduction

In this experiment you will separate and identify the cations in an unknown mixture. The possible ions are Ag⁺, Cu²⁺, Fe³⁺, Cr³⁺, Zn²⁺, and Ba²⁺. For the separation and detection of the cations, you will use the ability of these ions to form precipitates, to form complex ions, or to show amphoteric behavior (act as either an acid or a base). In the first week you do preliminary tests with each cation to discover each ion’s characteristic behavior. From the data obtained, you devise a scheme for separating and identifying this group of cations. In the second week you apply this scheme to the analysis of an unknown containing one or more of these cations.

1. Sparingly Soluble Salts

Some cations form relatively insoluble salts that precipitate out of aqueous solution. For example, chloride salts are generally soluble with the notable exceptions of the salts containing Ag⁺, Pb²⁺, and Hg²⁺. Similarly, most sulfate salts are soluble with the exceptions of BaSO₄, PbSO₄, Hg₂SO₄, and CaSO₄. The formation of a precipitate upon introduction of chloride or sulfate into solution is a positive test for Ag⁺ or Ba²⁺, respectively.

Many hydroxide salts are also quite insoluble. For example, the solubility of Fe³⁺ ions in basic solution is governed by the reaction:

\[
\text{Fe(OH)}_3 (\text{s}) \rightleftharpoons \text{Fe}^{3+} (\text{aq}) + 3 \text{OH}^- (\text{aq})
\]  

The corresponding equilibrium expression is:

\[
K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3
\]  

The \(K_{\text{sp}}\) of 6.3x10⁻³⁸ shows that Fe(OH)_3 is a very sparingly soluble salt under most conditions. Equation (2) can be solved for the solubility of Fe³⁺ ions in solution:

\[
\text{solubility} = [\text{Fe}^{3+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^3}
\]  

Therefore, solubility rapidly decreases as the solution becomes more basic, Figure 1.
For hydroxide concentrations greater than $10^{-11}$ M (pH > 3), Fe$^{+3}$ is relatively insoluble. Therefore, in a qualitative analysis scheme (or “qual scheme”) Fe$^{+3}$ may be removed from solution by making the solution basic, thereby precipitating Fe(OH)$_3$. The precipitate is easily removed from solution by centrifugation.

However, Fe$^{+3}$ is not the only cation you are testing that forms an insoluble hydroxide. Therefore, addition of base to a mixture may precipitate other metal hydroxides in addition to Fe(OH)$_3$. For example, if Zn$^{+2}$ is also present, the following reaction and relationships also hold:

$$
\text{Zn(OH)}_2 (s) \rightleftharpoons \text{Zn}^{+2} (aq) + 2 \text{OH}^-(aq)
$$

$$
K_{sp} = [\text{Zn}^{+2}] [\text{OH}^-]^2 = 3.0 \times 10^{-16}
$$

$$
\text{solubility} = [\text{Zn}^{+2}] = \frac{K_{sp}}{[\text{OH}^-]^2}
$$

At hydroxide concentrations greater than $10^{-6}$ M (pH > 8), both Fe$^{+3}$ and Zn$^{+2}$ are insoluble and coprecipitate as hydroxides, Figure 1. Using a weak base, it might be possible to adjust the pH to the range where Fe(OH)$_3$ precipitates but Zn(OH)$_2$ does not. A buffer solution is a better approach to pH control. However, in practice, careful control of the pH to selectively precipitate a given cation is difficult. Alternative approaches to separating Fe$^{+3}$ and Zn$^{+2}$ are either to use the amphoteric nature of Zn(OH)$_2$ or the ability of Zn$^{+2}$ to form complex ions as described below.

**II. Amphoteric Hydroxides**

Some hydroxide precipitates dissolve with excess hydroxide because of the formation of soluble hydroxo-complexes:

$$
\text{Zn(OH)}_2 (s) + 2 \text{OH}^- (aq) \rightleftharpoons [\text{Zn(OH)}_4]^{2-} (aq)
$$

Such hydroxides are called amphoteric hydroxides because they dissolve in both acid and base. The equilibrium constant for this reaction is favorable, $K_f = 2 \times 10^{20}$. Therefore, while Zn(OH)$_2$ forms on addition of small amounts of a strong base to a Zn$^{+2}$-containing solution, continued addition of strong base causes the precipitate to dissolve by formation of the [Zn(OH)$_4$]$^{2-}$ complex. Amphoteric behavior is useful in qualitative analysis. If excess base is added to a mixture of Fe$^{+3}$ and Zn$^{+2}$ ions, Fe(OH)$_3$ precipitates but the soluble [Zn(OH)$_4$]$^{2-}$ remains in solution; thus, a separation of Fe$^{+3}$ and Zn$^{+2}$ is achieved.

**III. Complex Ion Formation**

The formation of hydroxo-complexes of amphoteric hydroxides is useful for dissolving precipitates or for the prevention of precipitate formation. The formation of complexes other than hydroxo-complexes are also useful. For example, ammonia forms complex ions with Cu$^{+2}$:

$$
\text{Cu}^{+2} (aq) + 4 \text{NH}_3 (aq) \rightleftharpoons [\text{Cu(NH}_3)_4]^{+2} (aq)
$$

This reaction has a large equilibrium constant, $K= 4.8 \times 10^{12}$, showing that the formation of the [Cu(NH$_3$)$_4$]$^{+2}$ complex is quite favorable.

The utility of ammonia in separation schemes is shown by the behavior of a mixture of Fe$^{+3}$ and Cu$^{+2}$ ions. Remember that an ammonia solution is basic, since ammonia is a weak base:

$$
\text{NH}_3 (aq) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ (aq) + \text{OH}^- (aq)
$$
If concentrated ammonia is added to a solution containing Fe$^{3+}$ and Cu$^{2+}$ ions, Fe(OH)$_3$ precipitates in the presence of base (Eq. 1) and the complex ion [Cu(NH$_3$)$_4$]$^{2+}$ remains in solution; thus, a separation is achieved.

**IV. Oxidation-Reduction Reactions**

Oxidation reactions can also play a role in qualitative analysis. In the list of ions you are testing (Ag$^+$, Cu$^{2+}$, Fe$^{3+}$, Cr$^{3+}$, Zn$^{2+}$, and Ba$^{2+}$), only Cr$^{3+}$ is not in its maximum oxidation state in aqueous solution. Hydrogen peroxide generates a good oxidizing agent, OOH$^-$, in basic solution:

$$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{OOH}^- + \text{H}_2\text{O} \quad (10)$$

The result is that Cr$^{3+}$ is oxidized to soluble chromate ions (CrO$_4^{2-}$) in a basic solution containing hydrogen peroxide. Chromate ions are brightly colored, and therefore the oxidation of Cr$^{3+}$ is a good visual test for chromium.

**V. The Presence of Colored Ions**

A preliminary examination of an unknown that may contain a colored cation can yield valuable information. Three of the cations you are testing are colored. If the solution is colorless, these three ions are either absent or present in extremely low concentrations. Some caution is warranted, because mixtures of colored cations can be confusing. For example, if Fe$^{3+}$ and Cu$^{2+}$ are both present, the observed color is hard to predict.

**VI. Confirmatory Tests**

Separation schemes result in the identification of each cation. However, confirmatory tests are often added to verify the presence of cations. Confirmatory tests often produce highly colored precipitates or complexes that are characteristic of a given cation. For example, the addition of thiocyanate ion to a solution of Fe$^{3+}$ ions produces an intensely red solution containing the iron(III)thiocyanate complex, as you discovered in Experiment 1. Some confirmatory tests also do double duty, as separation steps and confirmation. For example, the precipitation of bright yellow BaCrO$_4$ is a useful separation and confirmation step (as long as sulfate is not present):

$$\text{Ba}^{2+} (\text{aq}) + \text{CrO}_4^{2-} (\text{aq}) \rightleftharpoons \text{BaCrO}_4 (s) \quad (11)$$

**Pre-Laboratory Assignment**

**Week 1**  
In addition to the usual pre-lab questions for the first week, please also write the balanced chemical reaction for each reaction given in Appendix 1 in your lab notebook. Remember to balance for both mass and charge.

**Week 2**  
Use your data from Week 1 to devise a scheme for separating and identifying the six possible cations. This scheme should take advantage of the solubility differences among the salts, hydroxides, and complexes, the redox properties of the cations, and the confirmatory tests. Select a scheme of separation and identification that is effective, that entails the fewest steps, and that achieves the cleanest separations. Your scheme should be presented as a flow diagram that references the appropriate balanced chemical reactions that you prepared for Week 1. For each solution in your scheme also indicate if the solution is acidic or basic at each stage (see Step 12, below). A sample separation scheme for a different set of cations and test reagents is shown in Figure 2 (with no balanced equations). A pre-lab question will also be assigned for your notebook.
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Figure 2. Sample qualitative analysis separation scheme.

Experimental Procedure

I. Techniques

Centrifuge: The centrifuge is used to speed up the separation of a precipitate from a liquid. When a mixture of solid and liquid is placed in a tube and rotated at high speed in a centrifuge, the more dense precipitate is forced to the bottom of the tube by a centrifugal force that is many times greater than the force of gravity. After centrifuging, the supernatant, or clear liquid above the precipitate, can easily be poured off or withdrawn with a capillary (Pasteur) pipette. The centrifuge may be damaged if allowed to run unbalanced. Therefore, before centrifugation, prepare another tube to balance the sample tube by filling it with water until the liquid levels in both tubes are the same. Insert the tubes in opposite positions in the centrifuge, then set the machine in motion. Usually, 30 seconds of centrifugation achieves effective separation of the solid from the liquid.

Vortex Mixers: These motorized mixers are used to ensure complete homogeneity after reagent addition. Place your test tube in the cup at the top and gently but firmly press down to achieve mixing.

Addition of Reagents: Always use a dropper or capillary pipette when adding a small quantity of a liquid to a test tube or other vessel. One mL is about 20 drops. If a reagent bottle has a dropper, replace it promptly after use. Do not allow the dropper to touch the container or solution to which you are adding the dropper’s contents. Do not set the dropper down on the benchtop or another surface, and be sure to return it to the correct bottle. If the bottle does not have a dropper, do not insert your own; instead, pour a small amount of reagent into a clean beaker, insert your dropper into that portion and discard the rest into a waste container. Be sure to clean your dropper before and after use. Always mix thoroughly after adding reagent.
Precipitation: To detect the formation of a precipitate on mixing two solutions, it is essential that both solutions be initially clear; if necessary, centrifuge to clarify. A “clear” solution is transparent but not necessarily colorless.

After adding a reagent to bring about precipitation, always test for complete precipitation, if the purpose is to separate one substance from another. Suppose, for example, that a solution contains 0.10 millimole of \( \text{Ba}^{+2} \). We add to this solution a few drops of dilute \( \text{H}_2\text{SO}_4 \), and the amount happens to contain 0.08 millimole of \( \text{SO}_4^{-2} \). We have thus produced 0.08 millimole of solid \( \text{BaSO}_4 \), but 0.02 millimole of \( \text{Ba}^{+2} \) remains in the supernatant liquid, because we did not add enough \( \text{H}_2\text{SO}_4 \) to precipitate all the \( \text{Ba}^{+2} \) as \( \text{BaSO}_4 \). This fact can be discovered by centrifuging and adding another drop of reagent (dilute \( \text{H}_2\text{SO}_4 \) in this case) to the clear supernatant. If precipitation is complete, no additional precipitate forms. However, if insufficient reagent was added the first time, the additional drop causes formation of more precipitate. If more precipitate is observed, add several more drops of reagent, centrifuge, and again test for completeness of precipitation. Repeat until no precipitate is formed on adding reagent.

After the precipitate and supernatant are separated, the precipitate is washed by adding a few drops of the washing reagent (usually water), mixing thoroughly with a stirring rod, centrifuging, and removing the washings with a capillary pipette. Two or more washings are generally necessary to prevent contamination of the precipitate. Failure to wash precipitates is one of the most common sources of error in qualitative analysis.

Transfer of Precipitates: The easiest way to transfer a residue from one container to another is to mix the residue with small amounts of washing liquid and pour the suspension quickly into the new container. Repeat this two or three times to get complete transfer. For small volumes, draw the suspension into a pipette for transfer.

Heating of Solutions: To avoid excessive evaporation on prolonged heating, use a water bath. Always stir when heating test tubes. To create a water bath, fill a 250 or 400 mL beaker three-quarters full of water and set it on a hot plate. Fit the aluminum test tube holder into the beaker. Heat the water to a gentle boil.

Adjusting Acidity: Always stir well when adding acid or base. To test the pH of the solution, apply a drop onto litmus paper placed on a watch glass. Never dip the paper into the solution.

II. Available Chemicals

<table>
<thead>
<tr>
<th>Standards</th>
<th>Test Reagents</th>
<th>For Confirmatory Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M AgNO\textsubscript{3}</td>
<td>3 M HCl</td>
<td>6 M acetic acid</td>
</tr>
<tr>
<td>0.2 M Cu(NO\textsubscript{3})\textsubscript{2}</td>
<td>6 M NH\textsubscript{3}</td>
<td>0.2 M K\textsubscript{4}Fe(CN)\textsubscript{5}</td>
</tr>
<tr>
<td>0.2 M Fe(NO\textsubscript{3})\textsubscript{3}</td>
<td>6 M NaOH</td>
<td>0.2 M KSCN</td>
</tr>
<tr>
<td>0.2 M Cr(NO\textsubscript{3})\textsubscript{3}</td>
<td>3 M H\textsubscript{2}SO\textsubscript{4}</td>
<td>0.1 M Ba(NO\textsubscript{3})\textsubscript{2}</td>
</tr>
<tr>
<td>0.2 M Zn(NO\textsubscript{3})\textsubscript{2}</td>
<td>3% H\textsubscript{2}O\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>0.1 M Ba(NO\textsubscript{3})\textsubscript{2}</td>
<td>15 M NH\textsubscript{3} (fume hood)</td>
<td></td>
</tr>
</tbody>
</table>

Chemical Hazards: Several of the cations are considered toxic at low concentration, including Ag\textsuperscript{+} and Ba\textsuperscript{2+}. (Silver solutions and salts are used in some antibiotic preparations). Concentrated acids and bases are corrosive. Good laboratory practice is required when handling reagents with a variety of chemical toxicities. Spills should be cleaned up immediately. Immediate washing with soap and water are required after contact with the skin. All solutions containing the cations must be disposed of in the supplied waste containers.
III. Development of the Separation Scheme-Week 1

You will study the properties of the individual cations Ag+, Cu²⁺, Fe³⁺, Cr³⁺, Zn²⁺, and Ba²⁺ to develop an analysis scheme. You will use individual solutions of known cations to run through the tests outlined below to see how each cation behaves. Record all of your observations (precipitates, dissolving of precipitates, colors, etc.) in your notebook. An example of the table you might use is given below.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Ag⁺</th>
<th>Cu²⁺</th>
<th>Fe³⁺</th>
<th>Cr³⁺</th>
<th>Zn²⁺</th>
<th>Ba²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td></td>
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<td></td>
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<tr>
<td>6 M NaOH</td>
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<td></td>
</tr>
<tr>
<td>6 M NH₃</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>excess NaOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 M NH₃</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>H₂O₂ + excess NaOH</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>K₄Fe(CN)₆</td>
<td></td>
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</tr>
<tr>
<td>H₂O₂, NaOH, Ba(NO₃)₂</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KSCN</td>
<td></td>
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</tr>
</tbody>
</table>

1. Carefully observe each cation solution, recording information about color and other properties that might be helpful in the later analysis of your unknown.

2. Precipitation of Chlorides with Dilute HCl. In a spot plate add 10 drops of each cation solution to a different well. To each cation add a few drops of 3 M HCl and record observations.
   Caution: Never treat chlorides with strong oxidizing agents. Chlorine gas may be produced.

3. Precipitation of Hydroxides. You will produce hydroxide precipitates of some of the cations; save these precipitates for later tests. For this step you use test tubes, not spot plates.
   a) To 10 drops of each cation solution, add 15 drops of water and 1 drop of 6 M NaOH solution. If no precipitate forms, test the solution with litmus paper. If the solution is still acidic, add 6 M NaOH until the solution is just basic. (Addition of too much NaOH may cause the amphoteric hydroxides to redissolve.) Observe each solution carefully.
   b) To 10 drops of each cation solution, add 15 drops of water and 1 drop of 6 M NH₃ solution and mix. If no precipitate forms, test the solution with litmus paper. If the solution is still acidic, add more 6 M NH₃ until the solution is just basic, then add two drops in excess. (Addition of too much NH₃ may cause the cations that form NH₃ complexes to redissolve.) Observe and record your observations.

Both of these steps should produce hydroxide precipitates for most of the cations. Keep only the test tubes where precipitates formed. Centrifuge the precipitates, discard the supernatant solutions, and proceed to the next step.

4. Amphoteric Nature of the Hydroxides: Excess NaOH. Amphoteric hydroxides dissolve in excess base. To the hydroxide precipitates from Step 3a, add 6 drops of 6 M NaOH solution. Vortex well to mix. Observe to see if the precipitate dissolves. Save your precipitates from Step 3b for further testing below (in part 11).
5. **Ability to Form Coordination Complexes with NH$_3$: Excess NH$_3$.** Test 10 drops of each original cation solution with litmus paper. If the solution is acidic, add 1 drop 6 M NH$_3$ to make the solution just basic (add more if necessary). Then add an additional 20 drops of 15 M NH$_3$ (in hood) with mixing. If the cation solution is initially neutral, add 20 drops of 15 M NH$_3$, with mixing. Note any changes.

6. **Precipitation of Sulfates with Dilute Sulfuric Acid.** In a spot plate add 10 drops of each cation solution to a different well. Test each cation with a few drops of 3 M H$_2$SO$_4$.

7. **Oxidation with Alkaline Hydrogen Peroxide.** Use test tubes again for this step. To 10 drops of each cation solution, add 6 M NaOH dropwise until the solution is just basic. Add another 6 drops of 6 M NaOH, then 10 drops of 3% H$_2$O$_2$. Mix well then heat for 3 minutes in a beaker of boiling water and mix again. Note the results that differ from Steps 2 and 3. (In this step some of the precipitates change color but do not dissolve. This color change is probably due to the thermal decomposition of the hydroxide to an oxide.) Save the test tube that originally contained 0.2 M Cr(NO$_3$)$_3$ for further testing in Part 10 below.

8. **Confirmatory Test for Zinc.** When added to a slightly acidic solution containing zinc ions, ferrocyanide, Fe(CN)$_6^{4-}$, properly called hexacyanoferrate(II), produces a whitish precipitate that is a satisfactory test for zinc. To observe this reaction, check the standard Zn(NO$_3$)$_2$ solution with litmus to make sure it is acidic. If it is not, add 6 M acetic acid dropwise until it is barely acidic. Add 5 drops of 0.2 M potassium ferrocyanide solution, K$_4$Fe(CN)$_6$, and mix. A white or off-white precipitate confirms the presence of zinc.

9. **Confirmatory Test for Copper.** Copper ions can be detected in very dilute solutions by forming the brick-red species Cu$_2$Fe(CN)$_6$. To observe this reaction, take the standard Cu(NO$_3$)$_2$ solution and test with litmus to ensure that it’s acidic. If necessary, add 6 M acetic acid, a few drops at a time, testing with litmus, until the solution is just acidic. Then add 2 drops of 0.2 M potassium ferrocyanide solution, K$_4$Fe(CN)$_6$, and mix well. A brick red precipitate confirms the presence of copper.

   **Important Note:** because copper and zinc both react with potassium ferrocyanide to produce a precipitate, the two must be separated in your scheme prior to using this test. If both are present in the solution of unknown, then the brick red precipitate formed by copper ions will undoubtedly mask the white precipitate formed by zinc ions.

10. **Confirmatory Test for Chromium.** Chromium is usually oxidized to chromate in qualitative schemes. The yellow color of chromate is very sensitive, but not completely conclusive. After oxidizing Cr$^{3+}$ to chromate and forming the yellow solution in Part 7 above, add 6 M acetic acid until the solution is barely acidic. Then add 10 drops of the Ba(NO$_3$)$_2$ test ion solution. Mix well. The precipitate should be yellow if CrO$_4^{2-}$ is present. If you are doing this test on a mixture of cations and you added excess sulfate earlier, some BaSO$_4$ (a white precipitate) also forms. To avoid this problem, if you do not have Ba$^{2+}$ in your unknown, it is not necessary to perform the separation step using sulfuric acid prior to this test. This test can also be used in your qualitative separation scheme if you need to precipitate CrO$_4^{2-}$ from solution. Just remember that this test doesn’t work with Cr$^{3+}$; you must oxidize Cr$^{3+}$ to CrO$_4^{2-}$ first.

11. **Confirmatory Test for Iron.** In Part 3b above, you added excess base and formed a reddish or brownish precipitate from the 0.2 M solution of Fe(NO$_3$)$_3$ [this precipitate is Fe(OH)$_3$]. Centrifuge and remove this supernatant. Wash the precipitate with 10 drops of deionized water and discard the washing after centrifuging again. To the precipitate of Fe(OH)$_3$ add
1 mL (20 drops) of 3 M H₂SO₄ solution. If the precipitate does not dissolve at once, heat it in the water bath until it does. Cool and add 4 drops of 0.2 M potassium thiocyanate (KSCN) solution. The deep red confirms the presence of iron(III). A pink color is not significant, since there is usually a trace of iron in the reagents used, sufficient to produce a pink color.

12. A Simple Example Separation: Mix 10 drops of Fe³⁺ test ion solution with 10 drops of Cu²⁺. Repeat the addition of excess NH₃ as described in step 5. Centrifuge the sample. Compare the results to your observation table. In a qual scheme this separation is diagrammed as:

\[ \text{Fe}^{3+}, \text{Cu}^{2+} \quad (\text{acidic}) \]
\[ \downarrow \quad \text{20 drps of 15 M NH}_3 \]
\[ \text{Fe(OH)}_3 (s) \quad \text{Cu(NH}_3)_4^{2+} (aq) \quad (\text{basic}) \]

Before you leave the laboratory, obtain a summary table from your instructor of the expected results for each of these tests. You must have correct information in order to develop your qualitative analysis scheme for next week. This scheme should outline the procedure that you will follow to separate each cation and confirm or deny its presence. Note that the relevant reactions are provided in Appendix 1.

As you develop your scheme, you must pay careful attention to the sequence of reactions you perform. For example, if you have already formed the soluble Cu(NH₃)₄²⁺ species, then you cannot add NaOH to precipitate Cu²⁺ as Cu(OH)₂. Include confirmatory tests in your scheme.

V. Identification of Compositions of Unknown Samples - Week 2

A. Testing Your Scheme
Prior to initiating work on an unknown, you should test your scheme on known mixtures of the cations to make sure it works. Make up a solution containing some of the standard cation solutions and then run through your proposed scheme to see if it successfully detects all of the cations present. Try some of the tests on a spot plate instead of in test tubes. Initial testing of your unknown with spot plate tests can quickly rule out some cations, so that the steps that are designed to separate these cations can be eliminated from your procedure for that particular sample. For example, if you add H₂SO₄ to your mixture in a spot plate and no precipitate appears, then there is no need to add it on a large scale to your unknown. Make sure to revise your separation scheme as necessary. Include approximate amounts and concentrations of test reagents in your final scheme.

B. Unknown Sample
Once you have successfully tested your scheme, you should begin analysis of your unknown. Before beginning your analysis, prepare a portion of each unknown for x-ray fluorescence analysis as described in Part C below.

When working with your unknown, start with 10 drops of each unknown and use about 5-10 drops of most reagents. Be sure that you do not need the supernatant before discarding it. Also, make certain that the total volumes do not exceed about 3 mL. Always test for complete precipitation; this precaution is especially important, since no one has previously worked on your scheme with this unknown to determine what quantities of reagents are needed. Also test the pH as the correct pH is vital for the success of many tests. Simplify your scheme as you go along. If you know that a certain cation is absent, either from spot plate tests or early steps in your scheme, then the steps involving that cation can be eliminated from your scheme.
For example, if a spot plate test shows that Ag\(^+\) is absent, don’t bother to add HCl to your unknown. In your lab notebook, keep track of all your observations, including the amounts and concentrations of the test reagents you used.

It is possible that the unknown solutions contain acid. When a basic reagent such as NH\(_3\) or NaOH is added to an acidic solution, no result is to be expected until enough reagent has been added to neutralize the acid. Test with litmus paper to be sure that you have made the solution basic before you draw any conclusions.

C. Confirmation Using X-ray Fluorescence Spectroscopy
To be completely confident of your qual scheme, you should verify your results using x-ray fluorescence. X-ray fluorescence works well for all the cations in this lab, except for Ag\(^+\) and Ba\(^{2+}\). The sensitivity for Ag\(^+\) and Ba\(^{2+}\) is less than the other cations, but then Ag\(^+\) and Ba\(^{2+}\) are the easiest cations to detect by the wet chemistry.

In x-ray fluorescence, a collimated beam of x-rays is directed upon the sample. The incident x-rays have sufficient energy to eject inner-core electrons from the atoms in the sample. For light elements and first-row transition elements, 1s-electrons can be ejected. The 1s-electrons are called K-shell electrons. For heavier elements, such as Ag and Ba, 2s and 2p-electrons are ejected. The 2s and 2p-electrons are L-shell electrons. The vacancies produced are unstable. Electrons from adjacent orbitals drop into the vacancies to decrease the energy of the atom. To conserve energy, x-rays are produced when the electrons change energy levels. This process is called x-ray fluorescence. The fluorescent x-rays are lower in energy than the exciting x-rays and have energies that are characteristic of the atomic energy level spacing of the atom. The fluorescent x-ray energies for a given shell increase with increasing atomic number, Z, Figure 3.

![Figure 3: X-ray fluorescence spectrum of a sample containing Ag\(^+\), Ba\(^{2+}\), Cr\(^{3+}\), Fe\(^{3+}\), Cu\(^{2+}\), and Zn\(^{2+}\). K-\(\alpha\) peaks are labeled. (A small peak for Co\(^{3+}\) is present at 6.93 keV overlapping with Fe K-\(\beta\).)
The horizontal axis is the x-ray energy in keV (kilo-electron volts). The vertical axis is the count of individual x-rays per second. K-shell x-rays are emitted with two different energies. The lower energy is the K-α and the higher the K-β x-ray.

At the beginning of the laboratory, to prepare a sample of your unknown, place 3-5 drops onto a small disk of filter paper. Label your sample with your initials on the sheet below the piece of filter paper. Instructions for use of the instrument will be available in the laboratory. Your lab instructor or student assistant will help you analyze your sample.

You must turn in a written assessment of your unknown to your instructor prior to viewing your x-ray fluorescence results.

**Report**

Provide a list of cations that you determined to be present in your unknown and a list of cations that you determined were absent based on your qualitative analysis scheme. Provide the results of the cations present based on x-ray fluorescence. If your “wet chemical” results differ from the spectroscopic results, other than perhaps Ag⁺ and Ba²⁺, discuss the errors that may have occurred. For example, which steps in your scheme were inconclusive or failed to provide the required separation and why? Attach a copy of the scheme that you used in your analysis. Make sure to include confirmatory tests and concentrations of all reagents. Attach the balanced equations from Appendix 1.

Your report should be written in complete sentences, but no formal introduction, theory, results, or discussion should be provided beyond the information requested in the previous paragraph.

**Literature Cited**

Appendix 1. Some Relevant Reactions (Unbalanced)

1. \( \text{Ag}^+ \text{(aq)} + \text{Cl}^- \text{(aq)} \rightarrow \text{AgCl} \text{(s)} \)
2. \( \text{Ag}^+ \text{(aq)} + \text{OH}^- \text{(aq)} \rightarrow \text{AgOH} \text{(s)} \)
3. \( \text{Cu}^{2+} \text{(aq)} + \text{OH}^- \text{(aq)} \rightarrow \text{Cu(OH)}_2 \text{(s)} \)
4. \( \text{Fe}^{3+} \text{(aq)} + \text{OH}^- \text{(aq)} \rightarrow \text{Fe(OH)}_3 \text{(s)} \)
5. \( \text{Cr}^{3+} \text{(aq)} + \text{OH}^- \text{(aq)} \rightarrow \text{Cr(OH)}_3 \text{(s)} \)
6. \( \text{Zn}^{2+} \text{(aq)} + \text{OH}^- \text{(aq)} \rightarrow \text{Zn(OH)}_2 \text{(s)} \)
7. \( \text{Cu}^{2+} \text{(aq)} + \text{NH}_3 \text{(aq)} + \text{H}_2\text{O} \rightarrow \text{Cu(OH)}_2 \text{(s)} + \text{NH}_4^+ \text{(aq)} \)
8. \( \text{Fe}^{3+} \text{(aq)} + \text{NH}_3 \text{(aq)} + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 \text{(s)} + \text{NH}_4^+ \text{(aq)} \)
9. \( \text{Cr}^{3+} \text{(aq)} + \text{NH}_3 \text{(aq)} + \text{H}_2\text{O} \rightarrow \text{Cr(OH)}_3 \text{(s)} + \text{NH}_4^+ \text{(aq)} \)
10. \( \text{Zn}^{2+} \text{(aq)} + \text{NH}_3 \text{(aq)} + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 \text{(s)} + \text{NH}_4^+ \text{(aq)} \)
11. \( \text{Cr(OH)}_3 \text{(s)} + \text{OH}^- \text{(aq)} \rightarrow \text{Cr(OH)}_4^- \text{(aq)} \)
12. \( \text{Zn(OH)}_2 \text{(s)} + \text{OH}^- \text{(aq)} \rightarrow \text{Zn(OH)}_4^{2-} \text{(aq)} \)
13. \( \text{Cu(OH)}_2 \text{(s)} + \text{NH}_3 \text{(aq)} \rightarrow \text{Cu(NH}_3)_4^{2+} \text{(aq)} + \text{OH}^- \text{(aq)} \)
14. \( \text{Zn(OH)}_2 \text{(s)} + \text{NH}_3 \text{(aq)} \rightarrow \text{Zn(NH}_3)_4^{2+} \text{(aq)} + \text{OH}^- \text{(aq)} \)
15. \( \text{Ba}^{2+} \text{(aq)} + \text{SO}_4^{2-} \text{(aq)} \rightarrow \text{BaSO}_4 \text{(s)} \)
16. \( \text{Cr(OH)}_4^- \text{(aq)} + \text{H}_2\text{O}_2 \text{(aq)} + \text{OH}^- \text{(aq)} \rightarrow \text{CrO}_4^{2-} \text{(aq)} + \text{H}_2\text{O} \)
17. \( \text{Zn}^{2+} \text{(aq)} + \text{K}^+ \text{(aq)} + \text{Fe(CN)}_6^{4-} \text{(aq)} \rightarrow \text{Zn}_3\text{K}_2[\text{Fe(CN)}_6]_2 \text{(s)} \)
18. \( \text{Cu}^{2+} \text{(aq)} + \text{Fe(CN)}_6^{4-} \text{(aq)} \rightarrow \text{Cu}_2\text{Fe(CN)}_6 \text{(s)} \)
19. \( \text{CrO}_4^{2-} \text{(aq)} + \text{Ba}^{2+} \text{(aq)} \rightarrow \text{BaCrO}_4 \text{(s)} \)
20. \( \text{Fe}^{3+} \text{(aq)} + \text{SCN}^- \text{(aq)} \rightarrow \text{FeSCN}^{2+} \text{(aq)} \)