

## Experiment 4: Qualitative Analysis of Cations<sup>1</sup>

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

### Introduction

In this experiment you will separate and identify the cations in unknown mixtures. The possible ions are  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ba}^{2+}$ . 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 your unknowns containing one or more of these cations.

### I. 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  $\text{Ag}^+$ ,  $\text{Pb}^{+2}$ , and  $\text{Hg}_2^{+2}$ . Similarly, most sulfate salts are soluble with the exceptions of  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ ,  $\text{Hg}_2\text{SO}_4$ , and  $\text{CaSO}_4$ . The formation of a precipitate upon introduction of chloride or sulfate into solution is a positive test for  $\text{Ag}^+$  or  $\text{Ba}^{+2}$ , respectively.

Many hydroxide salts are also quite insoluble. For example, the solubility of  $\text{Fe}^{+3}$  ions in basic solution is governed by the reaction:



The corresponding equilibrium expression is:

$$K_{\text{sp}} = [\text{Fe}^{+3}][\text{OH}^-]^3 \quad (2)$$

The  $K_{\text{sp}}$  of  $6.3 \times 10^{-38}$  shows that  $\text{Fe}(\text{OH})_3$  is a very sparingly soluble salt under most conditions. Equation (2) can be solved for the solubility of  $\text{Fe}^{+3}$  ions in solution:

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

Therefore, solubility rapidly decreases as the solution becomes more basic, Figure 1.

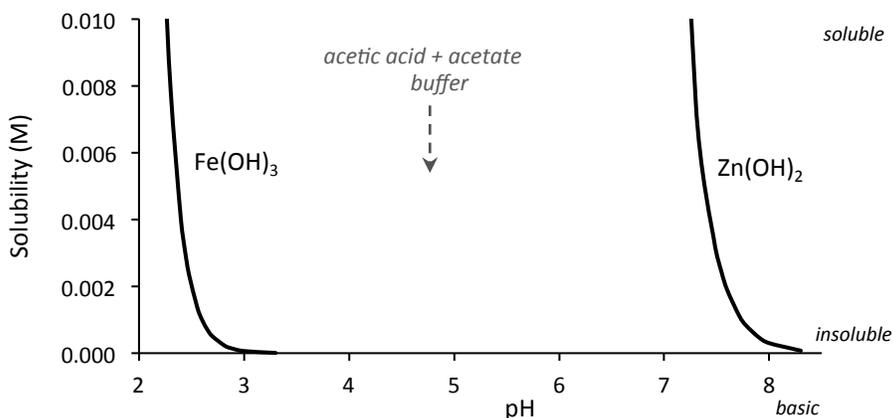


Figure 1: Solubility of  $\text{Fe}(\text{OH})_3$  and  $\text{Zn}(\text{OH})_2$  as a function of pH.

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

However,  $\text{Fe}^{+3}$  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  $\text{Fe}(\text{OH})_3$ . For example, if  $\text{Zn}^{+2}$  is also present, the following reaction and relationships also hold:



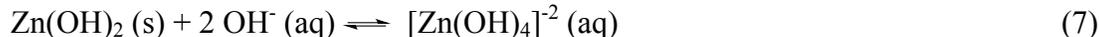
$$K_{\text{sp}} = [\text{Zn}^{+2}] [\text{OH}^-]^2 = 3.0 \times 10^{-16} \quad (5)$$

$$\text{solubility} = [\text{Zn}^{+2}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} \quad (6)$$

At hydroxide concentrations greater than  $10^{-6}$  M ( $\text{pH} > 8$ ), both  $\text{Fe}^{+3}$  and  $\text{Zn}^{+2}$  are insoluble and coprecipitate as hydroxides, Figure 1. Using a weak base, it might be possible to adjust the pH to the range where  $\text{Fe}(\text{OH})_3$  precipitates but  $\text{Zn}(\text{OH})_2$  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  $\text{Fe}^{+3}$  and  $\text{Zn}^{+2}$  are either to use the amphoteric nature of  $\text{Zn}(\text{OH})_2$  or the ability of  $\text{Zn}^{+2}$  to form complex ions as described below.

## II. Amphoteric Hydroxides

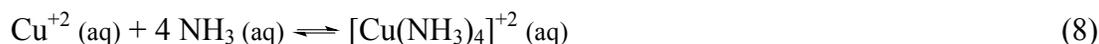
Some hydroxide precipitates dissolve with excess hydroxide because of the formation of soluble hydroxo-complexes:



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  $\text{Zn}(\text{OH})_2$  forms on addition of small amounts of a strong base to a  $\text{Zn}^{+2}$ -containing solution, continued addition of strong base causes the precipitate to dissolve by formation of the  $[\text{Zn}(\text{OH})_4]^{2-}$  complex. Amphoteric behavior is useful in qualitative analysis. If excess base is added to a mixture of  $\text{Fe}^{+3}$  and  $\text{Zn}^{+2}$  ions,  $\text{Fe}(\text{OH})_3$  precipitates but the soluble  $[\text{Zn}(\text{OH})_4]^{2-}$  remains in solution; thus, a separation of  $\text{Fe}^{+3}$  and  $\text{Zn}^{+2}$  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  $\text{Cu}^{+2}$ :



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

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



If concentrated ammonia is added to a solution containing  $\text{Fe}^{+3}$  and  $\text{Cu}^{+2}$  ions,  $\text{Fe}(\text{OH})_3$  precipitates in the presence of base (Eq. 1) and the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{+2}$  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 ( $\text{Ag}^+$ ,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{Cr}^{+3}$ ,  $\text{Zn}^{+2}$ , and  $\text{Ba}^{+2}$ ), only  $\text{Cr}^{+3}$  is not in its maximum oxidation state in aqueous solution. Hydrogen peroxide generates a good oxidizing agent,  $\text{OOH}^-$ , in basic solution:



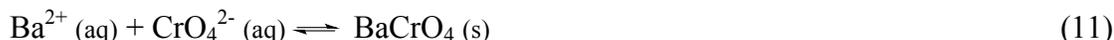
The result is that  $\text{Cr}^{+3}$  is oxidized to soluble chromate ions ( $\text{CrO}_4^{-2}$ ) in a basic solution containing hydrogen peroxide. Chromate ions are brightly colored, and therefore the oxidation of  $\text{Cr}^{+3}$  is a good visual test for chromium.

#### ***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  $\text{Fe}^{+3}$  and  $\text{Cu}^{+2}$  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  $\text{Fe}^{3+}$  ions produces an intense red solution containing the iron(III)thiocyanate complex, as you discovered in Experiment 2. Some confirmatory tests also do double duty, as separation steps and confirmation. For example, the precipitation of bright yellow  $\text{BaCrO}_4$  is a useful separation and confirmation step (as long as sulfate is not present):



## 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 upon 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 (provided in your fume hood). Always stir when heating test tubes. To create a water bath, fill the provided 250 or 400 mL beaker three-quarters full of water and set it on a hot plate in the fume hood. 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 paper towel. *Never dip the paper into the solution.*

## II. Available Chemicals

Standards	Test Reagents	For Confirmatory Tests
0.1 M AgNO <sub>3</sub>	3 M HCl	6 M HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> (acetic acid)
0.2 M Cu(NO <sub>3</sub> ) <sub>2</sub>	6 M NH <sub>3</sub>	0.2 M K <sub>4</sub> Fe(CN) <sub>6</sub> •3H <sub>2</sub> O
0.2 M Fe(NO <sub>3</sub> ) <sub>3</sub>	6 M NaOH	0.2 M KNCS
0.2 M Cr(NO <sub>3</sub> ) <sub>3</sub>	3 M H <sub>2</sub> SO <sub>4</sub>	0.1 M Ba(NO <sub>3</sub> ) <sub>2</sub>
0.2 M Zn(NO <sub>3</sub> ) <sub>2</sub>	3% H <sub>2</sub> O <sub>2</sub>	
0.1 M Ba(NO <sub>3</sub> ) <sub>2</sub>	15 M NH <sub>3</sub> (fume hood)	

Chemical Hazards: Several of the cations are considered toxic at low concentration, including Ag<sup>+</sup> and Ba<sup>2+</sup> (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.

## Week 1

### III. Development of the Separation Scheme

You will study the properties of the individual cations Ag<sup>+</sup>, Cu<sup>+2</sup>, Fe<sup>+3</sup>, Cr<sup>+3</sup>, Zn<sup>+2</sup>, and Ba<sup>+2</sup> 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. If a box is marked "X" then no observation is required for that combination.

	Ag <sup>+</sup>	Cu <sup>+2</sup>	Fe <sup>+3</sup>	Cr <sup>+3</sup>	Zn <sup>+2</sup>	Ba <sup>+2</sup>
<i>pH (acidic or basic):</i>						
<i>Initial color of solution:</i>						
Reagent	Ag <sup>+</sup>	Cu <sup>+2</sup>	Fe <sup>+3</sup>	Cr <sup>+3</sup>	Zn <sup>+2</sup>	Ba <sup>+2</sup>
HCl						
6 M NaOH						
6 M NH <sub>3</sub>						
excess NaOH						
15 M NH <sub>3</sub>						
H <sub>2</sub> SO <sub>4</sub>						

H <sub>2</sub> O <sub>2</sub> + excess NaOH						
K <sub>4</sub> Fe(CN) <sub>6</sub>	X			X		X
H <sub>2</sub> O <sub>2</sub> , NaOH, Ba(NO <sub>3</sub> ) <sub>2</sub>	X	X	X		X	X
KNCS	X	X		X	X	X

### QUALITATIVE SEPARATION TESTS

Before doing any tests: turn on the hot water bath to a medium heat and record the original color of each cation solution.

- HCl test:** *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; mix each with tip of plastic pipette then record observations. Rinse spot plate into sink and clean for reuse.

**Caution:** Never treat chlorides with strong oxidizing agents as chlorine gas may be produced.
- Hydroxide test:** *precipitation of hydroxides.*

A) In a set of 6 test tubes, each containing 10 drops of one of the cations, add 15 drops of water and 1 drop of **6 M NaOH** solution. Vortex. If no precipitate forms, test the solution with litmus paper adding 6 M NaOH until just basic. Too much NaOH may cause amphoteric hydroxide complexes to re-dissolve so do not add more to your precipitates. Observe and record what each solution looks like, before versus after. Bring the test tubes with precipitates to the centrifuge to spin for one minute then discard the supernatant from each (use a waste beaker). Keep the test tubes with precipitate for further testing. All other test tubes can be cleaned for reuse.

B) In a set of six clean test tubes, each containing 10 drops of one of the cations, add 15 drops of water and 1 drop of **6 M NH<sub>3</sub>** solution. Vortex. If no precipitate forms, test the solution with litmus paper and add 6 M NH<sub>3</sub> until just basic. Too much NH<sub>3</sub> may cause the cations that form NH<sub>3</sub> complexes to re-dissolve. Observe each solution carefully and record what each looks like, before versus after. Save only the test tubes with precipitate for further testing. All other test tubes can be cleaned for reuse.
- Excess hydroxide test:** *amphoteric nature of the hydroxides using excess NaOH.* Amphoteric hydroxide complexes will dissolve in excess base. To the hydroxide precipitates from Test 2A, add 6 more drops of **6 M NaOH** solution. Vortex. Observe to see which, if any, of the precipitates dissolve and record observations for each cation. The contents of these test tubes will not be used again, so empty each into your waste beaker. Clean test tubes for reuse.
- Excess ammonia test:** *ability to form coordination complexes using excess NH<sub>3</sub>.* Bring the hydroxide precipitates from Test 2B to the front fume hood to add 1 mL of **15 M NH<sub>3</sub>** and stir each with a plastic pipette. Note which cations do and do not undergo a change. The contents of these test tubes will not be used again, so empty each into the provided labeled waste container. Clean test tubes for reuse.

- Sulfate test:** *precipitation of sulfates with dilute sulfuric acid.* In a spot plate test each cation by adding a few drops of 3 M H<sub>2</sub>SO<sub>4</sub> to 10 drops of a cation solution in a different well. **Do not let the H<sub>2</sub>SO<sub>4</sub> dropper touch the cation solutions!** Mix with a plastic pipette and then record observations for all six cations. You may rinse the spot plate into sink. Clean the spot plate for reuse.
- Oxidation & heat test:** *oxidation with alkaline hydrogen peroxide.* To six clean test tubes, add 10 drops of each cation solution, then **6 M NaOH** until the solution is just basic. Add another 6 drops of 6 M NaOH, then 10 drops of 3% H<sub>2</sub>O<sub>2</sub>. Vortex. Record what each looks like. Heat for 3 minutes in a boiling water bath. Vortex. Record what each one looks like. 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 just the chromium test tube for the **Confirmation Test**. All other test tubes can be cleaned for reuse.

### QUALITATIVE CONFIRMATION TESTS

- Chromium:** This test can only begin with a sample that has completed the **Oxidation & heat test** first. Using the chromium test tube saved earlier, which oxidized Cr<sup>+3</sup> to chromate (CrO<sub>4</sub><sup>-2</sup>) and formed a yellow solution; add **6 M acetic acid** until it is *barely* acidic. Add 10 drops of the Ba(NO<sub>3</sub>)<sub>2</sub> ion solution. Vortex. A precipitate should be present and it should be yellow if CrO<sub>4</sub><sup>-2</sup> is present. Record your observation.

*More special notes concerning chromium:*

If you are doing this test on a mixture of cations and you added excess sulfate earlier, some BaSO<sub>4</sub> (a white precipitate) will also form. To avoid this problem, if you do not have Ba<sup>+2</sup> 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 analysis scheme if you need to precipitate CrO<sub>4</sub><sup>-2</sup> from solution. Just remember that this test doesn't work with Cr<sup>+3</sup>; you must oxidize Cr<sup>+3</sup> to CrO<sub>4</sub><sup>-2</sup> first.

- Zinc:** When added to a slightly acidic solution containing zinc ions, ferrocyanide [Fe(CN)<sub>6</sub><sup>-4</sup>, properly called hexacyanoferrate(II)] produces a whitish precipitate that is satisfactory as a test for zinc. To observe this reaction, put 10 drops of zinc solution into a test tube. Test the pH with litmus paper to make sure it is acidic. If it is not, add **6 M acetic acid** drop wise until it is barely acidic. Add 5 drops of **0.2 M potassium ferrocyanide solution** [K<sub>4</sub>Fe(CN)<sub>6</sub>] and mix. A white or off-white precipitate confirms the presence of zinc. Record your observation.
- Copper:** Copper ions can be detected in very dilute solutions by forming the brick-red species Cu<sub>2</sub>Fe(CN)<sub>6</sub>. To observe this reaction, put 10 drops of copper solution into a test tube. Test the pH with litmus paper to ensure that it's acidic. If necessary, add **6 M acetic acid**, a few drops at a time, testing with litmus paper, until the solution is just acidic. Then add 2 drops of **0.2 M potassium ferrocyanide solution** [K<sub>4</sub>Fe(CN)<sub>6</sub>] and vortex. A brick red precipitate confirms the presence of copper. Record your observation.

*Another note concerning this test:*

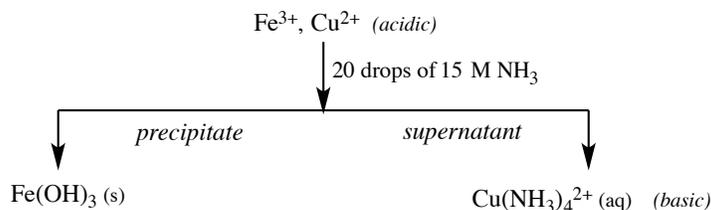
Try this test with Fe<sup>+3</sup>. Simply add about 10 drops each of the Fe(NO<sub>3</sub>)<sub>3</sub> solution and the potassium ferrocyanide solution to a test tube. Observe and record. What does this tell you about the importance

of separating ions prior to this test? Because multiple metal ions react with potassium ferrocyanide to produce a precipitate, these ions must be separated in your scheme prior to using this test. If two or more are present in the solution of unknowns, then any dark precipitate will undoubtedly mask any lighter colored precipitates formed by other ions.

- Iron:** Add ten drops of  $\text{Fe}(\text{NO}_3)_3$  solution to a spot plate well then add 4 drops of **0.2 M potassium thiocyanate** (KSCN) solution. Record your observation. A deep red color confirms the presence of iron(III) just as observed during Experiment #2.
- Silver:** of the six cations being tested only silver ions will form a whitish precipitate in the presence of chloride ions. If left to sit out for a while this precipitate will turn lavender in color (Separation Test #1).
- Barium:** of the six cations being tested only barium ions will form a whitish precipitate in the presence of sulfate ions (Separation Test #5).

Place your twelve cleaned test tubes in your lab drawer for reuse next week. Leave the spot plate and test tube rack on the lab bench. Rinse out used plastic droppers with DI water for re-use next week. Put these droppers in your lab drawer. Check that your hot plate has been turned off.

A Simple Example Separation: Mix 10 drops of  $\text{Fe}^{3+}$  test ion solution with 10 drops of  $\text{Cu}^{2+}$ . Repeat the addition of excess  $\text{NH}_3$  as described in step 4 of the Separation Tests section. Centrifuge the sample. Compare the results to your observation table. In a qual scheme, this separation is diagrammed as:



You must have correct information in order to develop your qualitative analysis scheme for next week. Your 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  $\text{Cu}(\text{NH}_3)_4^{2+}$  species, then you cannot add NaOH to precipitate  $\text{Cu}^{2+}$  as  $\text{Cu}(\text{OH})_2$ . Include confirmatory tests in your scheme.

## Week 2

### V. Identification of Compositions of Unknown Samples

#### 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  $\text{H}_2\text{SO}_4$  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 Samples

Once you have successfully tested your scheme, you should begin analysis of your two unknown cation mixtures. When working with your unknowns, **START WITH 10 DROPS** of each unknown (do not dilute with water initially) 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  $\text{Ag}^+$  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  $\text{NH}_3$  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.

### 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. Attach a copy of the scheme that you used in your analysis with each applicable reaction from Appendix 1 clearly noted at the appropriate location on the scheme. 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, procedure, results, or discussion should be provided beyond the information requested in the previous paragraph.

### Literature Cited

1. Adapted from an experiment by Rod O'Connor and Warren C. Woelfel, W. C., Freeman Library of Laboratory Separates in Chemistry, W. H. Freeman Company, San Francisco, 1971, *Vol. 11*, No. 1121.

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