

## Experiment 8

# Qualitative Analysis of Cations

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### PURPOSE

Identify which of the following ions are present in an unknown aqueous solution:  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ .

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### BACKGROUND

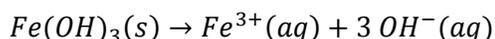
Before the development of modern spectrometry and chromatography, elaborate "wet chemistry" methods were necessary to separate and identify the components of a mixture. Up until the 1960s, second-year chemistry students took an entire course on qualitative analysis of metal ions. Although those methods are now only rarely used, they are still of value for their dramatic visual demonstrations of the effects that pH, temperature and other ions can have on the solubility and color of ionic compounds. The classic "qual scheme" is also a good exercise in deductive reasoning. The experiment below is what remains of EMU's old Qualitative Analysis course.

The basic idea of the qualitative analysis scheme is to exploit the variation in solubility of metal salts, such as chlorides, hydroxides, carbonates and sulfides. The concentrations of those anions, as well as certain Lewis-base complexing agents, are systematically adjusted. By comparing precipitate formation with known solubilities, the ingredients in the mixture can be deduced. In many cases, pretty colors of the dissolved, complexed or precipitated ions also help identification. The trick is to perform a sequence of chemical maneuvers that will

indicate the presence of each possible ion without interference from other possible ions.

Some of the important properties of the four cations to be studied in this experiment are summarized in Table I. Notice that some have more than one soluble form, and these may have different colors. Which form is present depends on what else is in the solution.

The  $K_{sp}$  values in Table I represent a way of describing solubilities that is more sophisticated than the solubility rules often taught in introductory courses. The  $K_{sp}$ , or solubility product, is the equilibrium constant for the formation of a saturated solution from an ionic solid. The smaller its value, the less soluble the compound (at the stated temperature). As an example, consider the dissolution of  $\text{Fe}(\text{OH})_3$  in water:



The  $K_{sp}$  for this reaction is

$$K_{sp} = [\text{Fe}^{3+}][\text{OH}^{-}]^3 = 4 \times 10^{-38} \quad (25^{\circ}\text{C})$$

The reactant concentration  $[\text{Fe}(\text{OH})_3(s)]$  is not seen in the denominator of this equilibrium constant, because the effective "concentrations" of pure solids are set equal to 1. The expression  $[\text{Fe}^{3+}][\text{OH}^{-}]^3$  is called the **solubility product**, and is analogous to the **reaction quotient, Q**. If the

**Table I. Properties of the ions to be analyzed.**

| ion              | Soluble form and its color                                       | K <sub>sp</sub> (25°C) and color of precipitate ion |                                     |                                 |                                |
|------------------|--|---|-------------------------------------|---------------------------------|--------------------------------|
|                  |  | hydroxide   | carbonate                           | chromate                        | oxalate                        |
| Fe <sup>3+</sup> | [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> reddish-brown | 4 x 10 <sup>-38</sup><br>rusty                      | soluble<br>grey                     | soluble                         | very soluble                   |
|                  | [FeCl <sub>4</sub> ] <sup>-</sup> yellow                         | soluble   |                                     |                                 |                                |
| Ni <sup>2+</sup> | [Ni(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> green         | 2 x 10 <sup>-14</sup><br>green                      | 7 x 10 <sup>-9</sup><br>light green | -----                           | 4 x 10 <sup>-10</sup><br>Green |
|                  | [Ni(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup> blue/lavender | soluble   |                                     |                                 |                                |
| Ba <sup>2+</sup> | Colorless  | 5 x 10 <sup>-3</sup>                                | 5 x 10 <sup>-9</sup><br>white       | 1 x 10 <sup>-10</sup><br>yellow | 2 x 10 <sup>-7</sup><br>white  |
| Ca <sup>2+</sup> | Colorless  | 6 x 10 <sup>-6</sup>                                | 3 x 10 <sup>-9</sup><br>white       | 7 x 10 <sup>-4</sup><br>yellow  | 2 x 10 <sup>-9</sup><br>white  |

reaction quotient is less than  $4 \times 10^{-38}$  when actual concentrations are used, the solution is unsaturated; additional solid would dissolve. Conversely, if it is greater than  $4 \times 10^{-38}$ , solid would precipitate out of solution. If it equals  $4 \times 10^{-38}$ , the solution is saturated.

Notice it is the product of both concentrations that is important: A very low concentration of one species can still cause precipitation if the other species has a very high concentration. For example, you can calculate that if [Fe<sup>3+</sup>] is 0.01 M, any [OH<sup>-</sup>] greater than  $2 \times 10^{-12}$  M should cause precipitation. This shows that careful control of acidity is an important part of a qual scheme, since [OH<sup>-</sup>] must also obey the following equilibrium constant, symbolized K<sub>w</sub>:

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \quad (25^\circ\text{C})$$

For the product of [H<sup>+</sup>] and [OH<sup>-</sup>] to equal a constant, acidic solutions, which have high [H<sup>+</sup>],

must have low [OH<sup>-</sup>]. Similarly, basic (alkaline) solutions, with high [OH<sup>-</sup>], must have low [H<sup>+</sup>].

Although K<sub>sp</sub> solubility calculations are more quantitative than predictions based simply on the solubility rules, they are subject to large errors: The K<sub>sp</sub> values depend somewhat on the concentration of "spectator" ions in the solution, and many ions have soluble forms besides those in the K<sub>sp</sub> reaction. It is risky to trust these calculations to more than one significant figure.

### IN THIS EXPERIMENT

A solution known to contain all four of the ions, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Ba<sup>2+</sup>, and Ca<sup>2+</sup>, and an unknown solution containing a subset of those ions will be analyzed. Reactions of the known solution will illustrate and verify the procedure. The composition of the unknown will be determined.

## PRE-LABORATORY PREPARATION

1. Read the background and procedure sections of the experiment.
2. On your Data Sheet, organize a system of headings, etc. that you will use to record all observations while doing the experiment. *You should record observations for both the known and unknown solutions after most procedure steps.*
3. Complete the computer-generated PRELAB assignment. Refer to the background and procedure sections of the experiment as needed.

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## EXPERIMENTAL SECTION

### REAGENTS PROVIDED

**Known and Unknown test solutions.** Contain 0.01 to 0.1 M of all four species:  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Ca}^{2+}$ .

**Analysis reagents.** All of the reagents needed will be provided in bottles with eye-dropper caps.

### HAZARDOUS CHEMICALS

Toxicologists have a saying: "The dose makes the poison." Literally any substance is toxic at sufficiently high doses. What constitutes prudent caution must be decided on a case-by-case basis. This experiment features a significant number of compounds that should be handled carefully at low exposures:

**6 M aqueous ammonia,  $\text{NH}_3(\text{aq})$ ; 6 M hydrochloric acid,  $\text{HCl}(\text{aq})$ ; and 6 M acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$**  are corrosive and toxic solutions. Prevent contact with your eyes, skin, and clothing. Keep capped to minimize inhaling vapors.

**Ammonium carbonate**, provided as **3 M  $(\text{NH}_4)_2\text{CO}_3(\text{aq})$** , decomposes in air to give ammonia. Used in "smelling salts."

**Barium ion**, provided as **0.1 M  $\text{BaCl}_2(\text{aq})$** , is highly toxic in soluble form. A massive dose of *insoluble*  $\text{BaSO}_4$  is used in the "barium swallow" intestinal x-ray procedure.

**Calcium chloride**, provided as **0.1 M  $\text{CaCl}_2(\text{aq})$** , and **potassium thiocyanate**, provided as **0.1 M  $\text{KSCN}(\text{aq})$** , are irritants.

**Chromium(VI)**, provided as **0.1 M  $\text{K}_2\text{CrO}_4(\text{aq})$** , is a suspected carcinogen.

**Dimethylglyoxime**, provided as **1 M DMG** solution in ethanol, is an irritant to eyes, mucous membranes and skin, and highly toxic

intraperitoneally. The ethanol solvent is classified as a depressant and irritant.

**Iron(III) chloride**, provided as **0.01 M  $\text{FeCl}_3(\text{aq})$** , is toxic and corrosive.

**Nickel ion**, provided as **0.01 M  $\text{NiCl}_2(\text{aq})$** , is toxic, an irritant, and a suspected carcinogen

**Oxalate ion**, provided as **0.2 M  $(\text{NH}_4)_2\text{C}_2\text{O}_4(\text{aq})$** , is toxic and an irritant. The reason rhubarb *leaves* are poisonous.

Do not touch your mouth after handling any of these chemicals. Wash your hands thoroughly before leaving the lab.

### WASTE DISPOSAL

Dispose of all wastes containing transition metal cations in the designated containers. You may need to break up solid wastes using your stirring rod and use a small amount of distilled water to rinse the precipitates into the waste containers.

### TECHNIQUES

#### READING LABELS

Nurses, and other workers who cannot afford to make label-reading mistakes, are taught a technique that chemists are also well-advised to use: Always look at every label three times. First, when you take the bottle from the shelf. Second, when you open the bottle. Third, when you return the bottle to the shelf.

The multiple brown bottles that all look alike represent a bounty of opportunities for mixups, any one of which will silently wreck the analysis. In the face of the wrong answer for your unknown, the instructors are not likely to be impressed by your claims that you followed the procedure exactly.

## CENTRIFUGATION

Centrifuges are dangerous. They can break the fingers of people who are over anxious, hurt the arms of people with dangling shirt cuffs, and scalp people with long loose hair. Never turn one on unless it is covered; never open the cover until it stops spinning.

**To assure proper balance, always load samples of equal weight opposite each other. Never run an odd number of samples- use a "dummy" tube containing a balancing amount of water.** An unbalanced machine will vibrate wildly (like an unbalanced washing machine) and possibly break the tubes. Sustained unbalanced operation will wreck the centrifuge bearings, and perhaps cause it to take a disastrous "walk" off the table.

Do not fill tubes so close to the top that there is a risk of sample slopping out. More than 3/4 full is asking for trouble.

## DECANTING SUPERNATANTS

The clear liquid over a settled precipitate is called the **supernatant**. It can usually be removed by gently pouring (decanting) it out, being careful not to lose any of the precipitate.

Some precipitates are too light and fluffy to settle well--even with centrifugation. In those cases, a sample of clear supernatant can usually still be obtained by constructing a filter-in-a-dropper, as follows:

- (a) Roll a thin wad of cotton (about 1 cm long) so one end forms a point. Insert the rolled point into the end of a clean glass dropper. Use enough cotton to give a snug fit, with a little unrolled cotton left hanging from the end. Do not use so much cotton that it will absorb and retain a lot of the supernatant you are trying to recover.
- (b) Compress the rubber bulb; immerse the cotton-plugged tip into the solution; and draw clear supernatant into the dropper.
- (c) Carefully holding the dropper on its side, so the contents do not drip out or roll up into the bulb, remove the cotton plug and express the contents into a clean tube.

## PROCEDURE

This entire experiment will be done individually. The centrifuges are to be shared on a first-come first-served basis; notice they can accommodate more than one person's samples at a time.

**AFTER PROCEDURE STEPS 5,7,8,9,13,15,16, and 17: Immediately record your observations on the Data Sheet for both known and unknown. *These should be descriptive of what is observed (e.g., a red precipitate forms, the solution turned yellow), as opposed to drawing a conclusion. Writing down observations is a good habit to develop. Incomplete observations will result in a poor grade even if the unknowns are identified correctly!***

## TEST SOLUTIONS

*Both the known and unknown test solutions should be carried through the complete analysis scheme. It is most efficient to analyze the samples side-by-side. This permits direct comparisons of test results, and generates balanced pairs of tubes for centrifugation. However, it presents more of an organizational challenge. Tubes can be labeled with tape wrapped around the top.*

1. **Add 15 drops of known cation test solution to a clean 13x100 mm test tube.**
2. **Present your instructor with a clean 13x100 mm test tube for your unknown test solution (about 15 drops).**

Immediately record your unknown number on the Data Sheet.

## PRECIPITATION OF IRON

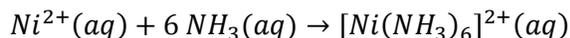
3. **Add 2 drops of 6 M HCl to each test solution.**
4. **Add 5 drops of 6 M NH<sub>3</sub> to each solution. Mix thoroughly using a glass stirring rod. (Use a separate stirring rod for each**

solution.) Test each solution to be sure that it is alkaline to litmus paper (red paper turns blue). To do this, use your stirring rod to transfer a clinging drop to the litmus paper (being careful that the drop represents your mixed sample).

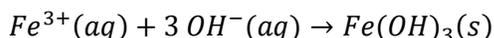
If the solution is still acidic, add another drop or two of 6 M NH<sub>3</sub> and retest.

**5. Add 5 more drops of 6 M NH<sub>3</sub> and thoroughly stir the solution.**

This neutralization of HCl by NH<sub>3</sub>, followed by addition of extra NH<sub>3</sub>, produces a mixture of NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> which effectively "buffers" the solution at a good alkalinity for precipitation of Fe(OH)<sub>3</sub>(s). Inspection of K<sub>sp</sub> values in Table I suggests that precipitation of nickel hydroxide also might be expected. However, because ammonia was used to make the solution alkaline, nickel ions have another option--formation of the very soluble ammonia complex [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>:



Thus, only Fe(OH)<sub>3</sub> should precipitate under these conditions:



If no precipitate forms, it can be assumed Fe<sup>3+</sup> was not present at detectable levels.

*If no precipitate formed in your unknown test solution, set it aside until you reach the precipitation of nickel, step 9.*

**6. If there is any indication of a precipitate (either settling out or remaining a cloudy suspension) centrifuge the sample for 1 minute. Decant (pour off) and save the supernatant into another labeled tube, to be used in step 9. Wash the precipitate by adding 15 drops of 6 M ammonia, agitating the precipitate with a clean glass rod, and recentrifuging for 1 minute. Decant and discard the washing supernatant.**

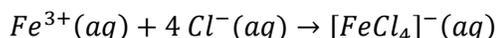
See the Techniques sections on Centrifugation and Decanting Supernatants, if necessary.

## CONFIRMATION OF IRON

Whenever possible, it is wise to do a confirmatory test to make sure a precipitate is not due to a contaminant. The K<sub>sp</sub> values indicate that if the solution has been made too basic, precipitation of nickel, calcium or barium hydroxides might give a false positive test for Fe<sup>3+</sup>.

**7. Dissolve the washed Fe(OH)<sub>3</sub> precipitate by adding five drops of 6 M HCl. Stir the solution with a clean stirring rod.**

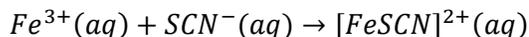
Notice if the expected color (Table I) appears as the iron complexes with chloride:



As this color might be faint and/or masked, we are fortunate to have a more specific and definitive test for iron.

**8. To the solution made in the previous step, add a volume of distilled water approximately equal to that already in the test tube. Add two drops of 0.1 M potassium thiocyanate (KSCN) solution, and stir.**

Formation of the characteristic deep-red thiocyanatoiron(III) complex [FeSCN]<sup>2+</sup> confirms the presence of Fe<sup>3+</sup>.

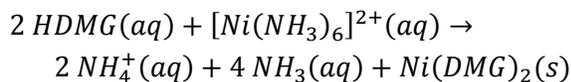


Dispose of this solution in the designated waste container.

## PRECIPITATION OF NICKEL

**9. Add ten drops of dimethylglyoxime (DMG) to each solution left after the iron precipitation procedure (either the solution from step 5 or the supernatant from step 6). Thoroughly stir the contents with a clean glass stirring rod for about 1 minute.**

Dimethylglyoxime has the formula (CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>(NOH)<sub>2</sub>. In basic solution, DMG has a particularly strong attraction for the nickel ion, prying it away from its ammonia complex, and forming the insoluble red compound that is diagnostic of nickel:



DMG is sufficiently specific for nickel so no additional confirmation is necessary.

If no precipitate formed in your unknown test solution, set it aside until you reach the precipitation of barium and/or calcium, step 13. If precipitate did form, it must be removed from the sample before the analysis can continue.

**10. Centrifuge the sample for 2 minutes to settle the precipitate as well as possible.**

**11. While waiting for the precipitate to settle, set up a boiling-water bath (for later use) by adding 200 mL of water to a 400-mL beaker and heating it with a Bunsen burner.**

**12. Use the dropper-filter technique (as described in the TECHNIQUES section on Decanting Supernatants) to transfer a clear sample of supernatant to a clean tube.**

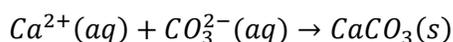
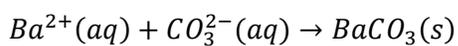
Since this  $\text{Ni}(\text{DMG})_2$  precipitate seldom completely settles enough for proper decantation, a filtration technique generally must be employed to obtain a sample of uncontaminated, clear supernatant.

One inch of liquid in a dropper should be enough to complete the analysis. Dispose of the  $\text{Ni}(\text{DMG})_2$  precipitate in the designated waste container.

## PRECIPITATION OF BARIUM AND/OR CALCIUM

**13. Add 15 drops of 3 M ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ ) to each solution left after the nickel precipitation procedure (either the solution from step 9 or the supernatant from step 12).**

Inspection of the  $K_{\text{sp}}$  values in Table I suggests that the carbonate salts of both of the two possible remaining ions, barium and calcium, should precipitate:

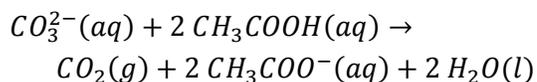
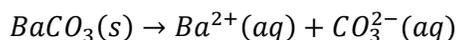


If no precipitate forms, you can conclude neither barium nor calcium are present, and you are done with the analysis. If a precipitate did form, continue as described below.

**14. Use a clean glass stirring rod to thoroughly mix the contents of the tube, then centrifuge for 1 minute. Decant and discard the supernatant. Wash the precipitate by adding 15 drops of distilled water, thoroughly stirring the contents again, and centrifuging again for 1 minute. Decant and discard the supernatant, and save the precipitate in the tube.**

**15. Add 5 drops of 6 M acetic acid to the precipitate. Heat the tube and its contents for 30 s in a boiling water bath. Stir the contents with a clean glass stirring rod. If necessary, add 2 additional drops of 6 M acetic acid to completely dissolve the precipitate. Once dissolution is complete, add 3 additional drops of 6 M acetic acid.**

All carbonates are soluble in acid because the carbonate ion is converted to  $\text{CO}_2$  which escapes as a gas. For example, in the presence of enough acid, the following reactions lead to the complete dissolution of  $\text{BaCO}_3(s)$ :



Heating assures the  $\text{CO}_2$  is driven out of the solution, so it cannot return to its carbonate form and cause problems later on.

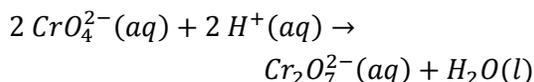
## PRECIPITATION OF BARIUM

**16. Add 15 drops of 0.1 M potassium chromate ( $\text{K}_2\text{CrO}_4$ ) to the solution formed in step 15. Stir the contents with a clean glass stirring rod. Heat the test tube and its contents for 1 minute in a boiling water bath. If there is any indication of a precipitate, while the mixture is still hot, centrifuge it for 1 minute. Decant and save the supernatant into a clean test tube for step 17.**

Turn off the bunsen burner so that the water bath can cool off while you finish the experiment.

If there is no precipitate (in the unknown) it is ready for step 17 (without the centrifugation). If there is a precipitate this indicates the presence of barium, subject to the disclaimer below.

This experimental step is a little touchy. The data in Table I indicate that although barium chromate is the more-expected precipitate, calcium chromate also is not highly soluble. Furthermore, the chromate ion is involved in another reaction that affects its availability for precipitation:



Notice how this interconversion of chromate and dichromate depends on the  $\text{H}^+$  concentration. If the acid concentration is too high, the reaction will be pushed to the right, possibly lowering the chromate concentration below that necessary to precipitate either calcium or barium. Conversely, if the acid concentration is too low, the reaction equilibrium will be shifted to the left, possibly raising the chromate concentration enough to precipitate both calcium and barium.

For those reasons, a weak acid (acetic acid) was used in step 15 to dissolve the carbonate(s). Even high concentrations of weak acids do not produce high concentrations of  $\text{H}^+$ .

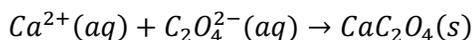
After decanting the supernatant, inspect the precipitate closely to see if it is the expected color. This is a little tricky because in this case the likely background color (from any remaining supernatant) is the same color. With those reservations, formation of a precipitate is taken as adequate proof of the presence of barium, and no additional confirmatory test is made.

Dispose of the  $\text{BaCrO}_4$  precipitate in the designated waste container.

## PRECIPITATION OF CALCIUM

**17. Add 10 drops of 0.2 M ammonium oxalate ( $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ) to the supernatant from step 16. Thoroughly stir the contents with a clean glass stirring rod. If precipitation occurs, centrifuge for one minute so the color of the precipitate can be assessed.**

Inspection of the  $K_{\text{sp}}$  values in Table I indicates that if calcium is present, it should precipitate as the oxalate salt:



Notice, however, that barium oxalate is also quite insoluble. If the barium concentration has not been sufficiently lowered by the previous step, a false positive test for calcium could result here. With that reservation, formation of a precipitate is taken as adequate proof of the presence of calcium, and no additional confirmatory test is made.

Dispose of both the supernatant, containing  $\text{CrO}_4^{2-}$ , and the  $\text{CaC}_2\text{O}_4$  precipitate into the designated waste container.

**18. Clean up your glassware. Dump any remaining precipitates in the designated waste containers. When you are through cleaning glassware, be sure to wash your hands thoroughly before leaving lab.**

**Caution:** Do NOT burn yourself on the hot water beaker, tripod, or wire gauze – they are hot! Let them cool before putting them away!

Name \_\_\_\_\_

Station Used \_\_\_\_\_

Instructor/Day/Time \_\_\_\_\_

\_\_\_\_\_  
Station Checked & Approved**DATA SHEET**

Record all relevant observations made during the experiment. You may use the back side of this page or additional sheets, if necessary. This will be turned in at the end of the lab.

| Step | Known | Unknown |
|------|-------|---------|
| 5    |       |         |
| 7    |       |         |
| 8    |       |         |
| 9    |       |         |
| 13   |       |         |
| 15   |       |         |
| 16   |       |         |
| 17   |       |         |

Circle all ions present in your unknown:  $\text{Fe}^{3+}$   $\text{Ni}^{2+}$   $\text{Ba}^{2+}$   $\text{Ca}^{2+}$

Unknown Number \_\_\_\_\_

On the back of this page (or an attached sheet), briefly explain (by referring to the relevant observations) how you could tell whether or not each of the ions was present in your unknown.