Experiment 8

Qualitative Analysis of Cations

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PURPOSE

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

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 Fe(OH)$_3$ in water:

$$Fe(OH)_3(s) \rightarrow Fe^{3+}(aq) + 3 OH^-(aq)$$

The $K_{sp}$ for this reaction is

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

The reactant concentration [Fe(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 $[Fe^{3+}][OH^-]^3$ is called the solubility product, and is analogous to the reaction quotient, $Q$. If the
Table I. Properties of the ions to be analyzed.

<table>
<thead>
<tr>
<th>ion</th>
<th>Soluble form and its color</th>
<th>K_{sp} (25°C) and color of precipitate ion</th>
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<tbody>
<tr>
<td>Fe^{3+}</td>
<td>[Fe(H_2O)_6]^{3+} reddish-brown</td>
<td>4 \times 10^{-38} rusty</td>
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<tr>
<td></td>
<td>[FeCl_4]^{-} yellow</td>
<td>soluble grey</td>
</tr>
<tr>
<td>Ni^{2+}</td>
<td>[Ni(H_2O)_6]^{2+} green</td>
<td>2 \times 10^{-14} green</td>
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<tr>
<td></td>
<td>[Ni(NH_3)_6]^{2+} blue/lavender</td>
<td>7 \times 10^{-9} light green</td>
</tr>
<tr>
<td>Ba^{2+}</td>
<td>Colorless</td>
<td>5 \times 10^{-3}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 \times 10^{-9} white</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>Colorless</td>
<td>6 \times 10^{-6}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 \times 10^{-9} white</td>
</tr>
</tbody>
</table>

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 $[\text{Fe}^{3+}]$ is 0.01 M, any $[\text{OH}^-]$ greater than $2 \times 10^{-12}$ M should cause precipitation. This shows that careful control of acidity is an important part of a qualitative scheme, since $[\text{OH}]$ must also obey the following equilibrium constant, symbolized $K_w$:

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

For the product of $[H^+]$ and $[OH^-]$ to equal a constant, acidic solutions, which have high $[H^+]$, must have low $[OH^-]$. Similarly, basic (alkaline) solutions, with high $[OH^-]$, must have low $[H^+]$.

Although $K_{sp}$ solubility calculations are more quantitative than predictions based simply on the solubility rules, they are subject to large errors: The $K_{sp}$ values depend somewhat on the concentration of "spectator" ions in the solution, and many ions have soluble forms besides those in the $K_{sp}$ 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^{3+}, Ni^{2+}, Ba^{2+}, and Ca^{2+}, 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.

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**PRE-LABORATORY PREPARATION**

1. Read the background and procedure sections of the experiment.
2. Complete the computer-generated PRELAB assignment. Refer to the background and procedure sections of the experiment as needed.
EXPERIMENTAL SECTION

REAGENTS PROVIDED

Known and Unknown test solutions. Contain 0.01 to 0.1 M of all four species: Fe$^{3+}$, Ni$^{2+}$, Ba$^{2+}$, and 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, NH$_3$(aq); 6 M hydrochloric acid, HCl(aq); and 6 M acetic acid, HC$_2$H$_3$O$_2$(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 (NH$_4$)$_2$CO$_3$(aq), decomposes in air to give ammonia. Used in "smelling salts."

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

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

Chromium(VI), provided as 0.1 M K$_2$CrO$_4$(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 FeCl$_3$(aq), is toxic and corrosive.

Nickel ion, provided as 0.01 M NiCl$_2$(aq), is toxic, an irritant, and a suspected carcinogen.

Oxalate ion, provided as 0.2 M (NH$_4$)$_2$C$_2$O$_4$(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, 10, 13, 15, 16, and 17: Immediately record your observations on the Data Sheet for both your known and unknown samples.

These should be descriptive of what is observed (e.g., a red precipitate forms, the solution turned yellow), as opposed to drawing a conclusion (e.g., Fe^{2+} is present).

Incomplete observations will result in a poor grade even if the unknowns are identified correctly!

PREPARATION OF TEST SOLUTIONS

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.

   Both the known and unknown test solutions should be carried through the complete analysis scheme, below. 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. Tubes can be labeled with tape wrapped around the top.
3. Add 2 drops of 6 M HCl to each test solution.

4. Add 5 drops of 6 M NH₃ 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 NH₃ and retest.

5. Add 5 more drops of 6 M NH₃ to each solution and thoroughly stir the solutions. Centrifuge both solutions for 1 minute. **Has a rusty-colored precipitate of Fe(OH)₃ formed?**

6. Decant (pour off) and save the supernatant into another labeled tube, to be used in step 9.

**IRON CONFIRMATION**

7. Wash the precipitate by adding 15 drops of 6 M ammonia, agitating the precipitate with a clean glass rod, and recentrifuge for 1 minute. Decant and discard the washing supernatant. Dissolve the washed Fe(OH)₃ precipitate by adding five drops of 6 M HCl. Stir the solution with a clean stirring rod. The solution should turn yellow, as the Fe(OH)₃ dissolves and [FeCl₄]⁻ forms.

8. To the solution made in the previous step, add a volume of distilled water approximately equal to that already in the test tube. Next, add two drops of 0.1 M potassium thiocyanate (KSCN) solution, and stir. Formation of the characteristic deep-red thiocyanatoiron(III) complex [FeSCN]²⁻ confirms the presence of Fe³⁺.

**IRON PRECIPITATION**

- **Yes**
- **No**

   If no precipitate forms, it can be assumed Fe³⁺ was not present at detectable levels.

   **NICKEL PRECIPITATION**

9. Add ten drops of dimethylglyoxime (DMG) to each solution left after the iron analysis (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.

10. Centrifuge the samples for 2 minutes. **While waiting, 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**

**Has a pink precipitate of Ni(DMG)₂ formed?**

11. Use the dropper-filter technique to transfer a clear sample of supernatant to a clean tube. See the TECHNIQUES section on Decanting Supernatants. One inch of liquid in a dropper should be enough. **Dispose of the solid in the designated waste container.**

- **Solid**
- **Supernatant**

If no precipitate forms, it can be assumed Ni²⁺ was not present at detectable levels.
BARIUM AND/OR CALCIUM PRECIPITATION

12. 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 10 or the supernatant from step 11).

13. Use a clean glass stirring rod to thoroughly mix the contents of the tube, then centrifuge for 1 minute.

Has a white precipitate formed?

Yes

No

14. Decant and discard the supernatant. Wash the precipitate by adding 15 drops of distilled water, thoroughly stir the contents, and recentrifuge for 1 minute. Again, 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.

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. Then centrifuge for 1 minute. Decant and save the supernatant into a clean test tube.

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

Solid

Supernatent

Formation of a yellow precipitate is taken as adequate proof of the presence of barium, and no additional confirmatory test is made.

Dispose of the BaCrO₄ precipitate in the designated waste container.

CALCIUM PRECIPITATION

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.

Formation of a white precipitate (it may look yellowish because of the yellow solution) is taken as adequate proof of the presence of calcium.

Dispose of both the supernatant, containing CrO₄²⁻, and the CaC₂O₄ 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!
EXPLANATION OF THE CHEMISTRY OCCURRING DURING THE PROCEDURE STEPS

Iron Precipitation: Steps 3-5.
This neutralization of HCl by NH₃, followed by addition of extra NH₃, produces a mixture of NH₄⁺ and NH₃ which effectively "buffers" the solution at a good alkalinity for precipitation of Fe(OH)₃(s). Inspection of K_sp 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(NH₃)₆]²⁺:

\[ Ni^{2+}(aq) + 6 \text{NH}_3(aq) \rightarrow [Ni(NH_3)_6]^{2+}(aq) \]

Thus, only Fe(OH)₃ should precipitate under these conditions:

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

Iron Confirmation: Step 8.
Formation of the characteristic deep-red thiocyanatoiron(III) complex [FeSCN]²⁺ confirms the presence of Fe³⁺.

\[ Fe^{3+}(aq) + \text{SCN}^-(aq) \rightarrow [FeSCN]^{2+}(aq) \]

Nickel Precipitation: Step 9.
Dimethylglyoxime has the formula (CH₃)₂C₂(NOH)₂. 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:

\[ 2 \text{HDMG}(aq) + [Ni(NH_3)_6]^{2+}(aq) \rightarrow 2 \text{NH}_4^+(aq) + 4 \text{NH}_3(aq) + Ni(DMG)_2(s) \]

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

Precipitation of Barium and/or Calcium: Step 12.
Inspection of the K_sp values in Table I suggests that the carbonate salts of both of the two possible remaining ions, barium and calcium, should precipitate:

\[ \text{Ba}^{2+}(aq) + CO_3^{2-}(aq) \rightarrow \text{BaCO}_3(s) \]
\[ \text{Ca}^{2+}(aq) + CO_3^{2-}(aq) \rightarrow \text{CaCO}_3(s) \]

Dissolving of the carbonates: Step 15.
All carbonates are soluble in acid because the carbonate ion is converted to CO₂ which escapes as a gas. For example, in the presence of enough acid, the following reactions lead to the complete dissolution of BaCO₃(s):

\[ \text{BaCO}_3(s) \rightarrow \text{Ba}^{2+}(aq) + CO_3^{2-}(aq) \]
\[ CO_3^{2-}(aq) + 2 \text{CH}_3\text{COOH}(aq) \rightarrow \text{CO}_2(g) + 2 \text{CH}_3\text{COO}^-(aq) + 2 \text{H}_2\text{O}(l) \]

Heating assures the CO₂ is driven out of the solution, so it cannot return to its carbonate form and cause problems later on.
Barium Precipitation: Step 16.

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:

\[ 2\text{CrO}_4^{2-}(aq) + 2\text{H}^+(aq) \rightarrow \text{Cr}_2\text{O}_7^{2-}(aq) + \text{H}_2\text{O}(l) \]

Notice how this interconversion of chromate and dichromate depends on the 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 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 BaCrO\(_4\) precipitate in the designated waste container.

Calcium Precipitation: Step 17.

Inspection of the K\(_{sp}\) values in Table I indicates that if calcium is present, it should precipitate as the oxalate salt:

\[ \text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \rightarrow \text{CaC}_2\text{O}_4(s) \]

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.
**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.

<table>
<thead>
<tr>
<th>Step</th>
<th>Known</th>
<th>Unknown</th>
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<tbody>
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<td>17</td>
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</tbody>
</table>

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

**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.