Experiment 12: QUALITATIVE ANALYSIS OF SELECTED CATIONS

Purpose: A sample containing one or more of the following ions is to be analyzed for its content: Ag\(^+\), Pb\(^{2+}\), Fe\(^{3+}\) and Cr\(^{3+}\).

Introduction: Qualitative Analysis refers to the determination of the presence of certain substances, as opposed to quantitative analysis, which refers to the determination of how much a certain substance is present. In this experiment you are examining for the presence of specifically four cations: Ag(I), lead(II), iron(III) and chromium (III). You will be given an unknown aqueous solution that contains one or more of these ions, and the objective is to determine which of them is/are present.

One of the problems you will face is co-precipitation. We know that Fe(OH)\(_3\) is a red-brown solid and Cr(OH)\(_3\) is a greenish-gray solid, and it would seem that we can easily identify the presence of Fe\(^{3+}\) and Cr\(^{3+}\) by the color of the two hydroxides formed. However, if OH\(^-\) was to be added to a solution containing both Fe\(^{3+}\) and Cr\(^{3+}\), the resultant mixture of precipitate would be grayish with perhaps a hint of green, depending on the concentration. The red-brown color of Fe(OH)\(_3\) would be masked by the color of Cr(OH)\(_3\). The solution to this problem is to physically either separate the Fe\(^{3+}\) and Cr\(^{3+}\) ions first before adding OH\(^-\), or separate the two hydroxides after they have formed.

Two of the key terms throughout experiment are “separate” and “identify.” In the process of the investigation you will be utilizing many of the concepts you have learned/are learning in the General Chemistry I and II lecture material: solubility (K\(_{sp}\)), complex ion formation, acid-base reactions, oxidation-reduction reactions, reactions of ammonia, working with net ionic equations, balancing redox equations under acidic or basic conditions. If you do not remember these concepts you should review the material by going to your General Chemistry textbook.

Brief Overview of the Qualitative Analysis Scheme
You should be familiar with the common solubility rules and recall that few ions will precipitate with the chloride ion. Silver(I) and lead(II) ions are two of the exceptions. Thus, when HCl is added to a solution containing the four cations (Ag\(^+\), Pb\(^{2+}\), Fe\(^{3+}\) and Cr\(^{3+}\)) for which you are testing, only AgCl and PbCl\(_2\) will precipitate out, leaving Fe\(^{3+}\) and Cr\(^{3+}\) in solution.

The two chloride precipitates are then separated by adding hot water. Of the two chlorides, PbCl\(_2\) is much more soluble. Hot water will dissolve only PbCl\(_2\), leaving AgCl as a solid.

The hot water containing Pb\(^{2+}\) is treated with potassium chromate and the formation of an orange-yellow PbCrO\(_4\) precipitate confirms the presence of the lead(II) ion.

The solid believed to be AgCl is re-dissolved by treating it with ammonia which complexes with the silver(I) ion to form Ag(NH\(_3\))\(_2\)\(^+\)(aq). PbCl\(_2\) will not form a complex. To confirm the presence of Ag\(^+\), acidify the solution with nitric acid. The nitric acid neutralizes the
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ammonia and shifts the equilibrium of the complex ion to the left, thus allowing AgCl to reform. The formation of a white precipitate confirms the presence of Ag⁺.

\[
\text{AgCl (s) + 2NH}_3 (aq) \rightleftharpoons \text{Ag(NH}_3)_2^+ (aq) + \text{Cl}^- (aq)
\]

Both the Fe³⁺ and Cr³⁺ will form insoluble hydroxides, Fe(OH)₃ and Cr(OH)₃. However, in excess OH⁻, Cr(OH)₃ will convert to the complex ion Cr(OH)₆³⁻. In the presence of hydrogen peroxide (3% H₂O₂), Cr³⁺ is converted to the chromate ion (CrO₄²⁻) by an oxidation-reduction reaction and goes into solution, leaving Fe(OH)₃ as a solid.

\[
\text{Cr}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{CrO}_4^{2-} + \text{H}_2\text{O} \quad [\text{not balanced}]
\]

The presence of Cr³⁺ is confirmed by adding barium chloride (BaCl₂) to the supernatant. Formation of a pale yellow BaCrO₄ precipitate provides the confirmation of the presence of Cr³⁺ in the unknown.

The presence of Fe³⁺ is confirmed by adding HCl to the Fe(OH)₃ precipitate. The hydrochloric acid neutralizes the hydroxide thus releasing the Fe³⁺ into solution, and by adding potassium thiocyanate (KSCN). The formation of a blood-red solution of FeSCN²⁺ complex confirms the presence of the Fe³⁺ ion.

**Important Terms and Techniques Relating to Qualitative Analysis:**

**THIS IS NOT A COOKBOOK-STYLE EXPERIMENT. YOU MUST UNDERSTAND THE CHEMISTRY BEHIND EACH STEP, KNOW EXACTLY WHAT YOU ARE DOING AND KNOW WHY YOU ARE DOING IT.**

**Supernatant:** When a precipitate formed from mixing two aqueous solutions together has settled to the bottom of the container, the solution above the precipitate is called the supernatant. It contains any ions that did not precipitate out.

**Centrifuge:** A centrifuge is an apparatus where samples are spun at a rapid speed so that the heavier particles are compressed to the bottom of the tube by centripetal acceleration. The centrifuges we are using typically have 6 to 8 slots in which to place test-tubes. It is used to aid us in separating a precipitate from the supernatant. If there is no sign of a precipitate, (no visible solid or cloudiness) there is no point in centrifuging the sample.

**Operating the Centrifuge Safely:**

- Make sure the centrifuge is sitting securely on the bench and not placed near the edge of the bench.
- Be sure your goggles are over your eyes.
- Always counter-balance the centrifuge by placing a test-tube containing about the same volume of water in the slot opposite to where your sample test-tube is placed.
- You will be sharing the centrifuge with other students. You can counter-balance with another student’s sample instead of water as long as the two are of about the same volume. Be sure you label your test-tubes with your initials so that you do not get them mixed up with those of other students.
- Follow instructions at the centrifuge as to the time and rpm settings to use.
Never try to stop the centrifuge with your hand. After you turn off the centrifuge, allow it to stop on its own.

**Separating the Supernatant from the Precipitate:** After centrifugation, tilt the test-tube at an angle and with a glass pipet, carefully remove the supernatant without disturbing the precipitate. It is important not to pick up any of the precipitate. It is better to err on the side of leaving a very small amount of liquid behind rather than drawing up some of the precipitate along with the supernatant.

**Washing the Precipitate:** In separating the supernatant from the precipitate there is bound to be some liquid remaining. To avoid contamination of the precipitate by this residual liquid, you will be asked to “wash” the precipitate with a reagent. This means adding the specified volume of reagent, stir or shake the contents of the tube thoroughly to mix, re-centrifuge and then remove the supernatant with a pipet.

**Testing for Complete Precipitation:** To ensure that all of the precipitate has formed, centrifuge so that all suspended solid is at the bottom of the tube, and then add a couple of drops of the specified reagent while watching to see whether the drops are causing the supernatant to become cloudy. Cloudiness is a sign that not enough of the reagent has been added. Do not confuse “swirls” with “cloudiness.” Swirls appear when two liquids of different densities are mixed and is not a sign of further precipitation. If you were to continue before precipitation is complete, the ions that should have precipitated out would remain in solution and can interfere with the test for other ions later on.

**Testing with Litmus Paper:** Red litmus paper will turn blue when in contact with a base and blue litmus paper will turn red when in contact with an acid. If you want to test whether a solution is acidic, you would NOT want to use red litmus paper because it cannot turn redder. Similarly, blue litmus paper cannot turn bluer. You must think about what color litmus paper is the appropriate one to use depending on whether you are testing whether a sample is acidic or basic.

The proper technique is to place a piece of litmus paper on a clean and dry watch glass. Wet the tip of a glass stirring rod with the solution you want tested and touch it to the litmus paper. DO NOT DIP THE LITMUS PAPER INTO THE SOLUTION YOU ARE TESTING. Also, do not place the litmus paper directly on the bench top as it is likely to become contaminated by chemicals from the bench top, as well as transfer acids and bases from the samples you are testing onto the bench top.

**Labeling test-tubes:** You should have a few blank labels handy and label the test-tubes as you go. Label them as P-2, S-2 etc. as necessary at each step. “P-2” refers to the precipitate formed at Step 2 and “S-2” refers to the supernatant formed at Step 2.

**Waste Beaker:** Label a 250-mL beaker as “Waste.” Dispose of all your chemicals in this waste beaker. At the end of the period you can empty it in the specified container in the hood.
Keeping Stirring Rods & Pipets Clean: By “stirring rod” we mean using the glass end of your stirring rod. Do NOT use the “rubber policeman” that is attached to the other end. By “pipet” we mean the *glass* Pasteur pipet with the thin tip and not the plastic ones.

Fill a clean 400-mL beaker with deionized water. Every time after use, rinse the stirring rods in the beaker of water. Pipets can be cleaned by emptying any residual solution into the waste beaker first (not into the clean water). Next, fill the pipet with water from the beaker of clean water and empty it into the waste beaker. Repeat three or more times, each time empty these subsequent rinses into the trough/sink as these rinses will contain only traces of the solutes. Replace the 400-mL beaker with fresh deionized water from time to time.

When adding reagents to a test-tube, do not let the dropper or pipet touch the walls of the test-tube as it will contaminate the dropper or pipet.

Although these pipets are “disposable” do not throw them out until you are finished with the experiment.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl (s)</td>
<td>white</td>
</tr>
<tr>
<td>AgCrO₄ (s)</td>
<td>rust brown</td>
</tr>
<tr>
<td>BaCrO₄ (s)</td>
<td>pale yellow</td>
</tr>
<tr>
<td>PbCl₂ (s)</td>
<td>white</td>
</tr>
<tr>
<td>PbCrO₄ (s)</td>
<td>orange-yellow</td>
</tr>
<tr>
<td>Pb(OH)₂ (s)</td>
<td>white</td>
</tr>
<tr>
<td>Cr(OH)₃ (s)</td>
<td>green</td>
</tr>
<tr>
<td>Fe(OH)₃ (s)</td>
<td>red-brown</td>
</tr>
<tr>
<td>FeSCN²⁺ (aq)</td>
<td>blood-red solution</td>
</tr>
</tbody>
</table>

SAFETY PRECAUTIONS IN HANDLING CHEMICALS

Wear your goggles at all times. Do not ingest any of the solutions. Wash your hands thoroughly if they come in contact with any of the chemicals in this experiment, especially before eating or drinking anything. The following chemical should be handled carefully. Avoid contact with eyes, skin and clothing:

- 6M HCl: toxic and corrosive, can cause burns, irritating vapors
- 6M HNO₃: can cause burns
- 6M NaOH: toxic and corrosive, can cause burns
- 6M NH₃: irritating vapors
- 0.2M AgNO₃: causes burns to eyes and skin, turns skin brown if in contact
- 1M K₂CrO₄: toxic, possibly carcinogenic
- 3% H₂O₂: can cause burns, will bleach clothing
- 0.1M KSCN: toxic
- 0.1M BaCl₂: toxic
**Procedure:**

WORK INDIVIDUALLY AND DO NOT EXPECT YOUR NEIGHBOR TO HAVE THE SAME OBSERVATIONS WHEN YOU ARE TESTING YOUR UNKNOWN!

FIRST GO THROUGH THE ENTIRE PROCEDURE WITH A “KNOWN” SOLUTION AND THEN REPEAT USING THE “UNKNOWN” ASSIGNED TO YOU.

The following procedure is written for a “known” solution, one that contains ALL four of the ions so that you can see what is to be expected for each ion. The observations described will therefore necessarily be different in certain steps for the unknown assigned to you as the unknown may not contain all four ions. Certain steps will have to be omitted accordingly. For example, if no precipitate is formed, there is no reason to centrifuge the solution.

**GETTING READY:**
- Obtain 2 glass Pasteur pipet and 4 test-tubes from the side-shelf. Do not use the test-tubes in your drawer as they are too big for the centrifuge. These test-tubes are more fragile than the regular test-tubes so handle them with care.
- Fill a 250-mL beaker half-full with deionized water and heat it over a hot plate. Place a glass pipet, tip-down, in the hot water. You can share the hot plate with another student, but do not share water baths as it is too easy to get samples mixed up.
- Prepare a known solution by adding 15 drops each of 0.2M AgNO₃, 0.1M Pb(NO₃)₂, 0.1M Fe(NO₃)₃ and 0.1M Cr(NO₃)₃ to a test-tube.

1. Add 15 drops of 6M HCl to the known and mix well with the use of your glass stirring rod. Wait 5 minutes while stirring the mixture occasionally. PbCl₂ is sometimes slow to form. Do not use metal spatulas or spoonulas in the entire procedure.
2. Centrifuge, add 2 more drops of 6M HCl and see whether the supernatant gets cloudy. If it does not mean not all of the Ag⁺ and/or Pb²⁺ have precipitated out and you will have to repeat step 2 until no more cloudiness is observed. Remember not to confuse “swirls” with “cloudiness” as discussed in the Introduction.
3. Next, with a glass Pasteur pipet, transfer the supernatant, which should contain Fe³⁺ and Cr³⁺, to a test-tube labeled S2. Do not disturb the precipitate (P2) which should contain AgCl and PbCl₂. (KEEP S2 IN A SAFE PLACE. YOU WILL WORK WITH IT LATER IN STEP 9.)
4. To P2 add 20 drops of water, stir well to mix and heat the sample in the boiling water bath. Stir occasionally. Remember PbCl₂ is soluble in hot water but AgCl is not. After 5 minutes, centrifuge (no more than 30 seconds) the t-tube containing the precipitate WHILE HOT. As soon as possible, use the hot pipet to transfer the hot supernatant (which should contain Pb²⁺ ions) into a clean t-tube labeled S4. The remaining precipitate is P4, which should be AgCl.
5. To confirm the presence of Ag⁺, wash P4 with 5 drops of hot water, centrifuge for 30 seconds, then add the wash liquid to S4.
6. To S4 add 5 drops of 1M K₂CrO₄. A yellow precipitate confirms the presence of Pb²⁺.
7. To P4, add 15 drops of NH₃. Mix well with a stirring rod. Check with litmus paper to see that it is basic. If not, add more NH₃ in 5 drop- aliquots until it is basic, stirring to
mix well. At this point P4 should mostly (if not entirely) have dissolved. Centrifuge and transfer the supernatant to another t-tube (S7). This supernatant should contain \( \text{Ag(NH}_3\text{)}_2^+ \). (PbCl\(_2\) will not dissolve in NH\(_3\). All of the AgCl in P5 should have dissolved and the silver is now in the form of Ag\(^+\) in the S7 solution. Any undissolved precipitate may be discarded. It is likely due to a trace amount of PbCl\(_2\) that did not dissolve fully.)

8. To S7, add 5 drops of 6M HNO\(_3\) to acidify the solution. Add more if necessary until it is acidic to litmus paper. The re-appearance of a white, lumpy precipitate confirms the presence of Ag\(^+\).

9. To S2, add 20 drops of 6M NaOH and mix well with a stirring rod. Check with litmus paper. If it is not basic, add more, in 5-drop aliquots until it is basic. A dirty brown gelatinous precipitate should form if Fe\(^{3+}\) and Cr\(^{3+}\) are present. Centrifuge and separate P9 (which contains red-brown Fe(OH)\(_3\) and green-grey Cr(OH)\(_3\)) from the supernatant. Discard the supernatant.

10. Next, to P9, add 10 drops of water, 10 drops of 6M NaOH and 15 drops of 3% H\(_2\)O\(_2\). Heat this mixture in a hot water bath (slightly below boiling) for 5 minutes or until sizzling stops (whichever comes first). Centrifuge and note the color of the supernatant (S10). If Cr\(^3+\) was present in the original unknown it has now been converted to CrO\(_4^{2-}\) which is yellow. If the supernatant is not yellow, add another 5 drops of H\(_2\)O\(_2\) and heat again until sizzling stops.

11. At this point the precipitate (P10) should look distinctively red, rather than a dirty brown. As long as any green or gray precipitate remains, you must continue to add more H\(_2\)O\(_2\) and heat the mixture. The H\(_2\)O\(_2\) should have converted all of the Cr\(^3+\) to yellow CrO\(_4^{2-}\) which is now in S10. The remaining precipitate should be the red-brown Fe(OH)\(_3\).

12. Centrifuge and transfer S10 to another t-tube. Add 5 drops of 0.1M BaCl\(_2\) to S10. The formation of a yellow precipitate confirms the presence of Cr\(^{3+}\).

13. To P10 add 6M HCl dropwise until it dissolves, then add 10 drops of water and 2 drops of 0.1M KSCN. An intense blood-red colored solution confirms the presence of Fe\(^{3+}\).

**ANALYSIS OF THE UNKNOWN:**

- Record the unknown number. **YOU WILL BE GIVEN A ZERO IF YOU FORGET TO RECORD THE UNKNOWN NUMBER AS WE WILL HAVE NO WAY OF KNOWING WHICH UNKNOWN YOU ANALYZED.**
- Start with clean water in your 400-mL beaker, wash all the glassware you used in your analysis of the known.
- Use 45 drops of the unknown and repeat starting at Step 1.
- Record observations carefully in your lab notebook.
- When drawing a conclusion on the unknown, report which cation/cations is/are present in the original unknown. For example, in Step 12, if a yellow precipitate forms, state that the unknown contains Cr\(^{3+}\). Do not state that the unknown contains CrO\(_4^{2-}\) even though the orange-yellow precipitate is PbCrO\(_4\), because originally, the chromium was present as Cr\(^{3+}\).
Flowchart of the Qualitative Analysis

Solution containing one
or more of the following:
Ag⁺, Pb²⁺, Fe³⁺, Cr³⁺

1. HCl

P2

AgCl, PbCl₂

4. Hot Water

P4

AgCl

7. NH₃

S7

Ag(NH₃)₂⁺

8. HNO₃

PbCrO₄

orange-yellow

AgCl

white

S9

Fe(OH)₃, Cr(OH)₃

discard

P9

K₂CrO₄

6. NaOH

S4

Fe³⁺, Cr³⁺

9. Fe(OH)₃, Cr(OH)₃

P10

Fe(OH)₃

BaCl₂

12. BaCrO₄

yellow

blood-red soln

HCl, KSCN

13. Fe(SCN)³⁻

Pre-Lab Assignment:

1. Preparation of notebook:
As usual, fill out the heading of the page and state the purpose of the experiment. There is not much to prepare as you will not know how much space to allot, and for the unknown you will not know exactly which steps in the procedure you will perform beforehand. However, you will need to keep careful notes as you do the experiment or you will get confused over which observations go with which step in the experiment, and at the end, draw the wrong conclusion.

As you perform the experiment you should write the Step number on the left half of the page, in accordance to the step number in the procedure, and add additional notes on what you did. This way you will not have to describe the whole procedure in your notebook. On the right half of the page, directly next to each step, record your observations and make use of the same notation (P2, S2, etc.) as in the procedure. (Do not invent your own.) In addition, jot down preliminary conclusions. When you reach a definite conclusion, circle it.

An example of how your lab notebook should look like is given on the next page.
Example of lab notebook entries:

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Observations/Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>4. P2 + 20 drops water, stirred &amp; heated.</td>
<td>All ppt dissolved. No AgCl. Ag⁺ absent in unknown.</td>
</tr>
<tr>
<td>5. skipped</td>
<td>No P4 as all dissolved in step 4.</td>
</tr>
<tr>
<td>6. S4 + 5 drops 1M K₂CrO₄</td>
<td>y ppt Pb²⁺ present in unknown.</td>
</tr>
</tbody>
</table>

2. In Step 1, if 6M HCl is added to an unknown and no precipitate is observed, what can you conclude about the unknown? Be precise and explain your answer.

3. If the unknown were to contain only Cr³⁺, in Step 10 after adding sodium hydroxide, hydrogen peroxide and heating for 5 minutes, what would you expect to see in the test-tube? Describe as precisely as you can what you expect to see, including color if any.

4. Write balanced net ionic equations for the following, including physical states:
   a) AgCl (s) + NH₃ (aq) →
   b) Ag(NH₃)₂⁺ (aq) + HNO₃ (aq) →
   c) Fe(NO₃)₃ (aq) + NaOH (aq) →
   d) Cr³⁺ (aq) + H₂O₂ (aq) → CrO₄²⁻ (aq) + H₂O (l)
      *Hint: Balance this as a redox reaction under basic conditions. (Review Section 5.2 in Brady & Senese, *Chemistry: Matter and Its Changes*, 5th edition, 2009.*
   e) Fe(OH)₃ (s) + HCl (aq) →
   f) Fe³⁺ (aq) + KSCN (aq) →

5. Explain in full sentences why you should not expect to see a precipitate in reaction 4a) or 4f) in Pre-Lab Question 4, even though the reactions will take place.

**Post-Lab Questions:**

1. On your own paper, write net ionic equations for the formation of each precipitate in the known. If multiple ions precipitate out in a single precipitate, you should write an equation for each ion. You will have 6 reactions total. Remember to include physical states.

2. Type a discussion and conclusion for the analysis of your unknown. First state the unknown number and the cations you have determined to be present. Next describe the step in the experiment that provided evidence of the presence of each of those ions. Then describe the steps that provided evidence of the absence of the other ions.
3. Mary Smith analyzed an unknown using the procedure described in this experiment. Upon adding 6M HCl to her unknown, a precipitate appeared. The cations in the unknown are all present as nitrates. (For example, Ag$^+$ if present is there as AgNO$_3$, Pb$^{2+}$ is present as Pb(NO$_3$)$_2$ etc.) Which of the following statement or statements is/are true of her unknown at this point of the analysis? (True or False?)
   a) Ag$^+$ must be in the unknown.
   b) Pb$^{2+}$ must be in the unknown.
   c) Both Ag$^+$ and Pb$^{2+}$ must be in the unknown.
   d) Either Ag$^+$ or Pb$^{2+}$ must be in the unknown.
   e) No conclusion can be drawn whatsoever.
List ALL the ions that MUST be in her S2 (including ions from test reagents).
List ALL the ions that are only POSSIBLY present in her S2.