Introduction to Qualitative Analysis

Chemical analysis can be either qualitative or quantitative in nature. In qualitative analysis we work to identify the substances present in a given sample. We are not concerned with the quantity of each substance, but only whether certain substances are present or absent. On the other hand, in quantitative analysis we are concerned with determining the amount of each component present in a sample. For example, those of you who took Chemistry 1A at Foothill College should remember that we prepared and then analyzed the "green crystals", K$_2$Fe(C$_2$O$_4$)$_3$(H$_2$O)$_2$. Qualitative analysis of this ionic compound could be used to reveal that iron, potassium and oxalate ions are present. It could also be used to determine that the iron is in its $+3$ oxidation state and that the substance is a hydrate. On the other hand, quantitative analysis of the green crystals would reveal that it contains 11.4% Fe$^{3+}$, 23.9% K$^+$, 53.7% C$_2$O$_4^{2-}$ and 11.0% H$_2$O by mass.

The techniques used in qualitative analysis depend upon the material being analyzed. For inorganic compounds, qualitative analysis often involves the identification of ions present in a sample. This is the type of analysis you will be involved with for your unknown; you will be given an aqueous solution containing a mixture of several metal cations that you must identify. The techniques you will learn can be used to identify ions occurring in other types of samples such as minerals, ground water and industrial waste streams. The procedures used will provide you with an opportunity to apply principles learned from your general chemistry lectures and textbook. These principles include those involved in acid-base chemistry, oxidation-reduction reactions, ionic equilibria, precipitation reactions and complex ion formation.

Focusing on our goal to correctly identify the metal cations that are present in our unknowns, the simplest scheme we can imagine would involve one that has a specific reagent to test for each different cation. In such a scheme, each reagent would be required to give an easily recognized confirmation test, such as color change or precipitate formation, for only one of the cations in the mixture, regardless of the other cations present. However, different metal cations can sometimes exhibit similar behavior and a specific reagent for each separate cation is not possible. In other words, individual components in our unknowns would most likely interfere with one another. Therefore, in the scheme that we will employ, reagents will be used to separate the ions in our samples into groups. Each group will then be analyzed for the presence or absence of individual metal cations. The most common way to subdivide into smaller groups is by selective precipitation, in which a small group of cations is chemically precipitated. The ions in the precipitate can then be physically separated from those remaining in solution by centrifuging. The precipitate (solid) settles out and the solution (supernatant) is transferred into another container. In this way, the initial large group is separated into smaller and smaller groups until definitive tests can be run to confirm the presence or absence of each specific cation.

The cations in our qualitative analysis scheme will be organized into groups that we will labeled A through D:

<table>
<thead>
<tr>
<th>Group</th>
<th>Cations in Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ag$^+$, Pb$^{2+}$</td>
</tr>
<tr>
<td>B</td>
<td>Mn$^{2+}$, Fe$^{3+}$, Bi$^{3+}$, Al$^{3+}$, Cr$^{3+}$</td>
</tr>
<tr>
<td>C</td>
<td>Ca$^{2+}$, Ba$^{2+}$, Sr$^{2+}$</td>
</tr>
<tr>
<td>D</td>
<td>Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Mg$^{2+}$</td>
</tr>
</tbody>
</table>

It is important to recognize the distinction between these groups and the groups of the Periodic Table (alkali metals, transition metals, etc.); the groups A-D do not necessarily correlate with groups in the Periodic Table. Periodic Table groups are based upon similarities in electron configurations that result in similar behaviors of the elements within the group. Some of the cations in our groupings do fall within the same Group in the Periodic Table, Group C for instance, and others do not, Group A for instance. The Groups we use in qualitative analysis are based solely upon the solubility behavior of the cations under specific conditions. For example, Group A consists of cations that form insoluble chlorides in acidic solution. Within each of these Groups, A-D, the analysis may require that there be further separations into subgroups. A specific or confirmatory test will be carried out for each ion when separations have ensured that interfering ions have been removed. Sometimes this will mean isolation of a given ion from all other cations. In other cases, it will be possible to carry out confirmatory tests in the presence of one or more other cations of the same group. To be successful, care must be taken to follow the procedures carefully; components that are not separated correctly may interfere with later tests.

As you work to identify the cations present in your unknown, you should follow directions carefully so that your analysis will be more likely to produce clear results. However, keep in mind that many different variables are at play in determining how a given sample will behave in the presence of each reagent used. You must be prepared for unexpected results, be observant and keep careful, accurate notes of your observations in your notebook. When confronted with ambiguity or uncertainty, do not despair! Rather, try to apply knowledge already gained about your sample to limit the possibilities. You may need to repeat experiments, possibly making modifications to the procedure or trying alternative tests WITH YOUR INSTRUCTOR’S APPROVAL. View this analysis as a type of puzzle that you must solve. You will be successful in solving the puzzle if you understand the background chemistry with which you are working, employ good techniques, carefully follow procedures, carefully observe and keep thorough notes. Before beginning your
Net-ionic equations
The reactions we will encounter take place in aqueous solution. Many of the reactions will occur between ions, including monatomic (e.g., Ag⁺, Cl⁻) and polyatomic ions (e.g. SO₄²⁻). Some may also involve the reaction of neutral molecules in solution. For writing NET IONIC chemical equations for reactions, the general guidelines are SUMMARIZED as follows:

1. Dissolved ionic compounds, the strong acids (HCl, HBr, HI, H₂SO₄, HNO₃ and HClO₄) and the strong soluble bases (Group 1A metal hydroxides) are completely dissociated/ionized in solution into the corresponding ions.
2. Water, gases, insoluble compounds, weak acids such as acetic acid (CH₃COOH) and weak bases such as ammonia (NH₃) will be present as neutral molecules.

The extent of chemical reactions and chemical equilibrium concepts
It is important to remember that many chemical reactions do not go to completion. The extent to which a reaction occurs depends on the magnitude of the equilibrium constant (K) for the reaction, and the relative amounts of reagents present. Equilibria can be shifted by adding or removing reactants or products, by adding other reagents and/or by changing the temperature, in accordance with Le Chatelier’s principle. By applying this principle, we can force precipitation to occur, cause some sparingly soluble compounds to dissolve, or complex particular ions so that they will not interfere with tests for other ions of interest.

Common reagents
Some common reagents and their uses in qualitative analysis are listed Table 1. You should become familiar with these reagents and their uses.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Effect on System and Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 M HCl</td>
<td>Raises [H⁺]; lowers [OH⁻]; dissolves insoluble hydroxides, carbonates, chromates and some sulfides; destroys hydroxo and NH₃ complex ions; increases [Cl⁻] causing precipitation of insoluble chlorides.</td>
</tr>
<tr>
<td>6 M NaOH</td>
<td>Raises [OH⁻]; lowers [H⁺]; precipitates insoluble hydroxides; forms hydroxo- complex ions.</td>
</tr>
<tr>
<td>6 M NH₃</td>
<td>Raises [OH⁻]; lowers [H⁺]; forms NH₃ complex ions; precipitates insoluble hydroxides; forms a basic buffer solution with NH₄⁺.</td>
</tr>
<tr>
<td>6 M HNO₃</td>
<td>Raises [H⁺]; lowers [OH⁻]; dissolves insoluble hydroxides, carbonates and chromates; destroys hydroxo and NH₃ complex ions; a good oxidizing agent when hot; dissolves insoluble sulfides by oxidation of sulfide ion.</td>
</tr>
</tbody>
</table>

REATIONS INVOLVED IN INORGANIC QUALITATIVE ANALYSIS
Several types of reactions encountered in qualitative analysis are discussed below along with examples of each.

Acid–Base Reactions
Acid-base reactions can be classified as Arrehinius, Bronsted-Lowry or Lewis. The following reactions are other examples of this diverse class.

\[
2\text{H}_2\text{O}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \leftrightarrow \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})
\]

\[
\text{Al(OH)}_3(\text{s}) + \text{OH}^-(\text{aq}) \leftrightarrow \text{Al(OH)}_2^-(\text{aq})
\]

\[
\text{Al(OH)}_3(\text{s}) + 3\text{H}_2\text{O}^+(\text{aq}) \leftrightarrow \text{Al}^{3+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})
\]

Compounds such as Al(OH)₃ that can react with either acid or base, are said to be amphoteric.
Buffers are a special case of acid-base reactions. A solution is said to be a buffer when it has approximately equal amounts of a weak acid or base and its conjugate salt. Common examples are \( CH_3COOH/CH_3COONa \) and \( NH_3Cl/NH_3 \). When buffered, a solution resists changes in pH when small amounts of a strong acid or base are added. The weak acid (or base) or the conjugate salt will react to absorb the added OH\(^-\) or H\(_2\)O\(^+\). Buffers are used as a means of controlling the pH, sometimes in order to regulate the nature of the species in solution. Consider the equilibrium between chromate (CrO\(_4^{2-}\)) and dichromate (Cr\(_2\)O\(_7^{2-}\))

\[
2H_2O^+(aq) + 2CrO_4^{2-}(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + 3H_2O(l)
\]

Dichromate salts tend to be soluble, whereas some chromate salts are not. Careful pH control using a buffer allows one to control the concentration of chromate ion in solution. We can therefore selectively precipitate specific metal cations as their insoluble chromates, leaving more soluble cations in solution.

Hydrolysis Reactions
Many ions or molecules react with water, resulting in the formation of either H\(_3\)O\(^+\) or OH\(^-\) ions, thus affecting the pH of the solution. This type of reaction, known as hydrolysis, is classified as acid-base. A common and important example is the hydrolysis of ammonia to form ammonium and hydroxide ions:

\[
NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)
\]

When acid is added to an ammonia solution, it reacts with ammonia, forming ammonium ion, shifting the equilibrium to the right, thus increasing the amount of NH\(_4^+\) in solution. The equilibrium can be driven to the left by heating to remove NH\(_3\) as gas. Adding a strong base will also shift the equilibrium to the left.

The concentration of the species undergoing hydrolysis has an effect on the pH. A solution of 0.1 M NH\(_3\) in water has a pH of 8.9, whereas a concentrated ammonia solution (14.5 M) has a pH of 10.0; an increase of hydroxide ion concentration by a factor of approximately 10. The concentration of ammonia can determine whether an ion precipitates as a hydroxide salt, forms a soluble ammonia complex, or doesn't react at all.

A second example of a hydrolysis reaction involves the oxalate ion (C\(_2\)O\(_4^{2-}\)):

\[
C_2O_4^{2-}(aq) + H_2O(l) \rightleftharpoons HC_2O_4^-(aq) + OH^-(aq)
\]

As pH increases the oxalate ion hydrolysis reaction shifts left, resulting in a higher concentration of oxalate ion. On the other hand, as pH decreases, the equilibrium shifts right and the concentration of oxalate ion decreases. Oxalate can be used to precipitate certain metal cations as their in soluble or slightly soluble oxalate salts. The pH of the solution upon addition of oxalate ion can determine if a precipitate will form or not.

Precipitation Reactions
The solubility product constant is related directly to the solubility of a sparingly soluble compound. Tables of \( K_{sp} \) values are available and are valuable resources for qualitative analysis. Familiarly with the general solubility rules is also helpful. A table of \( K_{sp} \) values (Table 2) and one of general solubility rules (Table 3) is provided. Study these and become familiar with them. When the ion product (Q\(_{sp}\)) of ions in solution exceeds the solubility product constant (\( K_{sp} \)) of a particular salt, precipitation will occur. Determining the presence of a precipitate is not always trivial. Some solutions become cloudy, which indicates a precipitate has formed. In some cases, you may be able to see grains of solid failing from solution. In other cases, the solution may become milky in appearance. The solution and the precipitate may or may not change color. The presence of a precipitate may be difficult to detect when a solution is dark. In such cases, centrifuging the solution to determine if a precipitate is present may help. A note on terminology: clear means not cloudy, colorless means uncolored (like water). The two terms are not synonymous.

The solubility of a particular species may be affected by adding reagents that cause a competing reaction. For instance, silver chloride, AgCl, is insoluble in deionized water, but can be made to dissolve by adding aqueous ammonia. This is due to the extremely favorable formation of the soluble silver ammonia complex, Ag(NH\(_3\))\(_2^+\):

\[
AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)
\]

\[
Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)
\]
Formation of the complex ion lowers the concentration of silver ion in solution, causing the first reaction to proceed further to the right, thus allowing more AgCl solid to dissolve.

**Decomposition Reactions:**
A decomposition reaction occurs when one chemical species decomposes into one or more different products. An example is the fizzing that results when acid is added to a carbonate:

\[
2\text{H}_2\text{O}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \\
\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})
\]

The carbonate ion undergoes an acid-base reaction, producing carbonic acid. Carbonic acid is very unstable, and spontaneously decomposes into water and carbon dioxide gas. The evolution of carbon dioxide from solution causes the fizzing, and shifts both equilibria further to the right.

**Oxidation-Reduction Reactions**
Oxidation-reduction, or redox, reactions are often accompanied by color changes and are used frequently in qualitative analysis to confirm the presence or absence of an ion. Redox reactions are also used as a means of dissolving very insoluble compounds and for converting an ion to a different oxidation state, in which case it may be more easily separated or identified. In the following example, pale green chromium (III) hydroxide, Cr(OH)$_3$, can be separated from a mixture of hydroxide solids, where its pale color is often masked, by oxidizing it using hydrogen peroxide, H$_2$O$_2$, in basic solution to form the chromate ion, CrO$_4^{2-}$. In solution, the chromate ion is bright yellow.

\[
\text{Cr(OH)}_3(\text{s}) + 4\text{OH}^-(\text{aq}) + 3\text{H}_2\text{O}_2(\text{aq}) \rightleftharpoons 2\text{CrO}_4^{2-}(\text{aq}) + 8\text{H}_2\text{O}(\text{l})
\]

The most common oxidizing agents are nitric acid, HNO$_3$, and basic hydrogen peroxide solution. Reducing agents include the ferrous [iron(II), Fe$^{2+}$], stannous [tin(II), Sn$^{2+}$], thiosulfate (S$_2$O$_3^{2-}$), oxalate (C$_2$O$_4^{2-}$), and iodide (I$^{-}$) ions. Hydrogen peroxide in acidic solution is also used as a reducing agent.

**Disproportionation** (self-redox) reactions are a special case of redox reactions wherein part of the reagent is oxidized, and an equivalent part, according to the stoichiometry, is reduced. An example is the spontaneous decomposition of hydrogen peroxide where oxygen, in the −1 oxidation state in peroxide, disproportionates into oxygen gas and water:

\[
2\text{H}_2\text{O}_2(\text{aq}) \rightleftharpoons \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})
\]

Hydrogen peroxide solutions will degrade over time due to this reaction. To slow the process and increase the shelf life of the solution, hydrogen peroxide solutions may be stored in a refrigerator.

**Formation of Complex Ions**
Many common anions and neutral molecules can donate one or more lone pairs of electrons, thus acting as Lewis bases to a Lewis acid. A coordinate covalent bond (one where both electrons are provided by one atom) is formed between the Lewis acid and the Lewis base. Certain metal cations act as Lewis acids. This type of reaction can result in the formation of a complex ion, an ion formed by a central metal cation bonded to from two up to six lone pairs of electrons on surrounding Lewis base species. In a complex ion, the Lewis bases are known as ligands. Water and ammonia are examples of neutral ligands. Anions that readily act as ligands include F$^-$, Cl$^-$, Br$^-$, I$^-$, SCN$^-$, C$_2$O$_4^{2-}$, OH$^-$, and CN$^-$. Metal cations in aqueous solution tend to have a fixed number of water molecules acting as ligands, although the water molecules are often not included when writing reactions. Square brackets, [ ], are often used to indicate the complex ion. For example, the following:

\[
\text{CuSO}_4(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})
\]

should more correctly be written as

\[
4\text{H}_2\text{O} + \text{CuSO}_4(\text{s}) \rightarrow [\text{Cu(H}_2\text{O)}_4]^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})
\]

The presence of water, or other ligands, causes many of the transition metal ions to be colored in solution. When a new ligand that has a higher affinity for the metal ion is added to a solution containing a complex ion, ligand replacement often
occurs. A new complex ion forms, often accompanied by a change in color of the solution. The color of the solution after adding a particular ligand is often a diagnostic test for the presence of a given metal cation. This is a common way of confirming the presence or absence certain cations in solution. Formation of a complex ions can also be used to dissolve a precipitate or to prevent a reaction of a certain cation with a reagent being used to test for or separate a different cation. For example, the Group B cations will be precipitated as hydroxide salts by adding ammonia. Three of the Group D cations (Cu$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$) do not precipitate under these conditions due to formation of complex ions with ammonia. A table of various complex ions (Table 4) is provided for your reference. It is valuable to become familiar with the complex ions that are listed in the table.

LABORATORY TECHNIQUES USED IN INORGANIC QUALITATIVE ANALYSIS

Cleanliness
Make sure that all test tubes and stirring rods are clean. Rinse the test tubes with deionized water and shake out as much of the liquid as possible before use. Rinse stirring rods before using them. Rinse droppers before reusing them for a different solution. For dispensing standard reagents (HCl, NaOH, NH$_3$, HNO$_3$) that are repeatedly used, label a dropper and dedicate it to a single reagent.

Adding Reagents
Use clean droppers. Some liquid reagents may be dispensed from bottles equipped with dropper caps. Be sure to replace the cap on the correct bottle. Screw it on firmly if it is a screw cap. Never place the tip of a dispensing dropper into your test solution in the test tube. Insert the tip about 0.5 cm below the top of the test tube, and release the indicated number of drops.

Mixing
If a small amount of liquid is present in a test tube, it may be mixed by flicking the base of the test tube with a finger while holding the test tube lightly by the top. Never shake a test tube that is capped with a finger or cork. Getting chemicals on fingers is an excellent means of introducing them into your body. Even if gloves are used, using a finger to cap a test tube is an easy means of contaminating other solutions. Also, if a test tube is capped with a finger or a cork, pressure may build up due to the evolution of heat or a gas in the test tube. Pressure build up can cause chemicals to spray out of the test tube. If the flicking technique is unsuccessful, or if the test tube is more than one-third full, a glass stirring rod should be used to mix the contents. Unless otherwise directed, always mix thoroughly after adding each reagent before making observations, checking pH or proceeding to the next step.

How to Describe Mixtures
Always describe the color and clarity of mixtures and reagents before mixing and what the mixture looks like after mixing, heating, centrifuging, etc. For example the following might be recorded for the separation of Group A cations from Groups B-D:

- Starting unknown solution-clear and colorless
- 6 M HCl-clear and colorless
- Add 10 drops of the HCl to the unknown solution and stir mixture. A cloudy white, precipitate formed.
- After centrifuging, white precipitate settles to bottom, clear and colorless supernatant.

Centrifuging
Be sure that the test tubes in use are the appropriate size for the centrifuge. A tube of approximately the same mass in the opposite slot of the centrifuge must be used to balance the centrifuge. This is easily accomplished by using a test tube of the same size, which is filled to approximately the same height with water. If you are simultaneously testing a known and an unknown, they can usually be used to balance each other. Other test tubes in the centrifuge may be of different masses, but each opposite pair should be matched. If the centrifuge is too unbalanced, it may "walk" around the countertop while it is spinning. Be sure that test tubes being centrifuged are neither cracked nor chipped. The stress applied by the centrifuge can cause damaged test tubes to shatter, resulting in chemicals and pieces of glass being scattered inside the centrifuge. A centrifuge without a top is dangerous; always close the top. Do not slow centrifuges down with your hands. They are spinning at a high rate of speed, and if there is any imperfection on the spinning surface, it can catch the flesh and do a great deal of damage in only an instant. Long hair must be tied back to avoid tangling in the centrifuge.
Decanting
After centrifuging, the supernatant is usually decanted into a clean test tube. Carefully tip the test tube, and pour off the supernatant without disturbing the pellet of solid. It may be poured directly, or a stirring rod may be placed across the mouth of the test tube to direct the supernatant into a clean test tube. If the supernatant has some solid still floating in it, it may be clarified in the following manner: Twist a very small piece of clean cotton and insert it into the end of a clean dropper leaving a tuft on the outside. Draw the supernatant up through the cotton, remove the cotton using tweezers, and release the clear supernatant into a clean test tube. The small amount of precipitate on the cotton is discarded.

Washing a Precipitate
After separation from the supernatant, a precipitate is often washed to free it from reagents that might interfere at a later stage. Usually, the rinse is deionized water, but other liquids or solutions may be used. Add the indicated amount of the wash liquid and stir the contents of the test tube thoroughly. The pellet of solid must be broken up and mixed well with the wash liquid. After thorough stirring, centrifuge the sample and decant the wash solution.

Heating
Due to the small quantity of material being heated, test tubes containing samples should NEVER be heated directly in a flame. A solution in test tube can reach its boiling point within a few seconds, and may be ejected violently from the test tube. All heating should be done using a water bath on a hot plate. Be careful that the tops of the test tubes are well above the water. The water may be boiling at times and could spatter into the test tubes, contaminating the contents.

Testing pH
When directed to check the pH of a solution, stir the solution thoroughly with a clean glass stirring rod and then touch the tip of the rod to a piece of pH paper. Several such tests may be performed on each strip of paper. Never insert the test paper into the test tube, since the chemicals on the paper could contaminate the contents.

General Safety Tips
Add all reagents gradually. Heat may be evolved, and the solution could become hot enough to boil. This is most likely to occur when neutralizing strong acids and bases. If a gas is evolved, such as when dissolving a carbonate solid in acid, the solution could bubble out of the test tube. Never situate a test tube so the open end is pointing at anyone. Never smell the contents of a test tube directly. If directed to check an odor, hold the test tube about 15 cm from your face, and gently waft any fumes from the top of the test tube toward your nose.

SEPARATION OF CATION GROUPS A, B1, B2, C, and D
To separate the cations into smaller groups, we must answer the following questions: What reagents should we use? What order should they be used in? How much of each reagent should we use? To answer these questions, the solubility product constants of various precipitates of these cations must be examined. It is useful to consider the formation constants of various complex ions formed by the metal cations as well. The separation scheme historically used in qualitative inorganic analysis is based on the solubilities of the metal chlorides and sulfides. In the historical scheme, the metal cations are divided into five groups, numbered Groups I, II, III, IV, and V. Group I is separated out as insoluble chlorides, while groups II and III are precipitated as insoluble sulfides. The precipitating agent originally was H₂S, a toxic and foul smelling gas. Later modifications of this method generated H₂S more safely by using thioacetamide. This was somewhat of an improvement, but thioacetamide is classified as a carcinogen and still has a foul smell. In this laboratory, neither material is used, thus avoiding some potential safety and environmental problems.

Table 2 lists the K_{sp} values of precipitates and some solubility behaviors we will consider in this qualitative analysis scheme. The cations are organized according to the subgroups used in the procedure. The object is to select reagents and conditions that result in the precipitation of a small group of cations that can then be tested. A partial flowsheet of the separation procedure is shown in Figure 1. You are required to draw this flowsheet in your lab notebook, filling in the missing information.

Group A: The Insoluble Chlorides
From Table 2, we find that a small group, Ag⁺ and Pb²⁺, are the only subset of cations that form insoluble chlorides. To separate this group, we need only add a source of chloride ions to the solution. Any chloride could be used, but the best is aqueous hydrochloric acid, since it does not add any other metal cations. It has the further advantage of making the concentration of hydroxide ion very low, preventing the possible coprecipitation of any hydroxide or oxide of the Group B-D
ions. Further separation of the Group A cations from each other is based on the chemistry of this smaller group and is discussed later in the Group A analysis experiment.

**Group B: Hydroxides Insoluble in Aqueous Ammonia**

Of the remaining cations we find that many of them form insoluble hydroxides. On closer inspection, note that they can be subdivided based on hydroxide solubility in NH₃ and oxidizing alkaline (for example, NaOH/H₂O₂) solution. The Group B cations are a rather large group, (Mn²⁺, Fe³⁺, Bi³⁺, Al³⁺ and Cr³⁺), all of which have hydroxides (or oxides) that are insoluble in NH₃ solution. After the Group B cations are precipitated and separated by centrifuging, they are further subdivided into subgroups B1 (Mn²⁺, Fe³⁺ and Bi³⁺) and B2 (Al³⁺ and Cr³⁺). This subdivision is based on the fact that the hydroxides of subgroup B1 remain insoluble in oxidizing alkaline solution whereas the cations of subgroup B2 are soluble in oxidizing alkaline solution due to formation of soluble hydroxide or oxide complexes. In the case of Cr³⁺, H₂O₂ in alkali is used as an oxidizing agent to convert chromium (III) hydroxide, Cr(OH)₃, to the soluble chromate ion, CrO₄²⁻. The separation of the Group B cations is summarized as follow:

1. By maintaining the pH between 9-10 (using a NH₃/NH₄⁺ buffer), the hydroxides of all Group B cations are precipitated. The Group C and Group D cations remain in solution, to be dealt with later.
2. The precipitate containing the Group B cations is then treated with a combination of 6 M NaOH and H₂O₂. This dissolves the subgroup B2 cations.
3. The precipitate containing the Group B1 cations is then treated with hot water to destroy any remaining H₂O₂ followed by further analysis to confirm the presence or absence of each ion.
4. The supernatant from step 2 is also heated to destroy any remaining H₂O₂, followed by further analysis to confirm the presence or absence of each ion.

**Group C:**

Next the group C cations (Ca²⁺, Sr²⁺ and Ba²⁺) are to be separated from the Group D cations by precipitation. You will be given the task of devising a separation and analysis scheme for this group. To start, you will need to select a precipitating agent. You will be directed to use information from Table 2 to guide you in your analysis scheme.

**Group D: Hyroxides and Oxides Soluble in Ammonia but Insoluble in NaOH**

After Groups A, B, and C are removed, the Group D cations remain in solution. Since three of the Group D cations form soluble ammonia complex ions, it is necessary to first remove any NH₃ that might be present in solution before analyzing the Group D supernatant. The presence of ammonia might interfere with later steps in the analysis. If oxalate is present from a previous step, it must also be removed to avoid interference. Ammonia and oxalate can be simultaneously removed through decomposition by evaporation of the solution to dryness, in a crucible, over a low flame. Upon heating ammonia is eliminated as a gas and any oxalate present is converted to CO₂ which is also eliminated as a gas. A small quantity of concentrated HNO₃ is then added to the cooled crucible and the contents heated to dryness once again to complete the decomposition. The Group D cations remain behind as solid oxides. This oxide precipitate is dissolved in HCl and then the solution is analyzed to confirm the presence or absence of each Group D cation.

**General Considerations**

Your unknown will be provided as an acidic solution. As you proceed through the analysis, you will at times need to store your unknown part way through the analysis and continue with it during the next lab period. When storing your unknown, keep the following in mind:

- It is best to keep unknown solutions as acidic solutions when possible. The metal cations are generally more stable in acidic solution. In basic solution, they may precipitate out as hydroxides, oxides or carbonates (see below).
- If you must keep a basic solution from one lab period to the next, stopper it tightly to prevent air oxidation of the solution and absorption of CO₂. Absorption of CO₂ by a basic solution may result in the formation of insoluble carbonates.
- If you must store a precipitate between lab periods, do not allow it to become dry. It should be centrifuged, washed and stored under deionized water in a stoppered test tube.
- Keep all unknown vessels labeled, with corresponding notations in your laboratory notebook. Failure to label or improper labeling of sample and/or reagents is a major source of poor results in qualitative analysis.
Table 2: $K_{sp}$ Selected $K_{sp}$ values and solubilities at temperatures around room temperature, from 18 to 25°C*

<table>
<thead>
<tr>
<th>Precipitating Agents</th>
<th>Cation</th>
<th>$Cl^-$</th>
<th>$OH$</th>
<th>$C_2O_4^{2-}$</th>
<th>$SO_4^{2-}$</th>
<th>$CO_3^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group A:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>1.8x10^{-10}</td>
<td>1.5x10^{-8}</td>
<td>1.3x10^{-11}</td>
<td>1.5x10^{-5}</td>
<td>8.1x10^{-12}</td>
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<tr>
<td>Pb$^{2+}$</td>
<td>1.7x10^{-5}</td>
<td>1.2x10^{-15}</td>
<td>2.7x10^{-11}</td>
<td>6.3x10^{-7}</td>
<td>7.4x10^{-14}</td>
<td></td>
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<tr>
<td><strong>SubGroup B1:</strong></td>
<td>soluble</td>
<td>i alkali</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>s</td>
<td>1.6x10^{-13}</td>
<td>i</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>s</td>
<td>4x10^{-38}</td>
<td>s</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Bi$^{3+}$</td>
<td>s</td>
<td>insoluble</td>
<td>s</td>
<td></td>
<td></td>
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<tr>
<td><strong>SubGroup B2:</strong></td>
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<td>s alkali</td>
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<td></td>
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<tr>
<td>Al$^{3+}$</td>
<td>s</td>
<td>1.3x10^{-33}</td>
<td>s alkali</td>
<td>s</td>
<td></td>
<td></td>
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<tr>
<td>Cr$^{3+}$</td>
<td>s</td>
<td>1.6x10^{-30}</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Group C:</strong></td>
<td>soluble</td>
<td>i in NH$_3$(aq)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>s</td>
<td>5x10^{-3}</td>
<td>1.6x10^{-6}</td>
<td>1.1x10^{-10}</td>
<td>5.0x10^{-9}</td>
<td></td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>s</td>
<td>6.5x10^{-6}</td>
<td>2.6x10^{-9}</td>
<td>2.4x10^{-4}</td>
<td>4.5x10^{-9}</td>
<td></td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>s</td>
<td>3.2x10^{-4}</td>
<td>1.6x10^{-8}</td>
<td>2.9x10^{-7}</td>
<td>9.3x10^{-10}</td>
<td></td>
</tr>
<tr>
<td><strong>Group D:</strong></td>
<td>soluble</td>
<td>s NH$_3$/NH$_4^+$</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Mg$^{2+}$</td>
<td>s</td>
<td>1.6x10^{-12}</td>
<td>8.6x10^{-5}</td>
<td>s</td>
<td>3.5x10^{-8}</td>
<td></td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>s</td>
<td>4.8x10^{-20}</td>
<td>s NH$_4^+$</td>
<td>s</td>
<td>2.3x10^{-10}</td>
<td></td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>s</td>
<td>6.0x10^{-16}</td>
<td>s NH$_4^+$</td>
<td>s</td>
<td>1.3x10^{-7}</td>
<td></td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>s</td>
<td>3.0x10^{-16}</td>
<td>s NH$_4^+$</td>
<td>s</td>
<td>1.0x10^{-10}</td>
<td></td>
</tr>
</tbody>
</table>

*Abbreviations: i = insoluble s = soluble alkali = NaOH NH$_3$/NH$_4^+$ = buffer pH 9-10

Table 3: General solubility rules for some common ions in aqueous solution

1. All nitrates (NO$_3^-$) are soluble.
2. Salts of Group 1A cations, the alkali metals, are soluble.
3. Ammonium (NH$_4^+$) salts are soluble.
4. Halides (Cl$^-$, Br$^-$ and I$^-$) are soluble, with some exceptions. Two common exceptions are Ag$^+$ and Pb$^{2+}$.
5. Sulfates (SO$_4^{2-}$) are soluble, with some exceptions. Three common exceptions are Pb$^{2+}$, Ba$^{2+}$ and Sr$^{2+}$. (Ca$^{2+}$ and Ag$^+$ are somewhat soluble.)
6. Permanganates (MnO$_4^-$) are soluble. The permanganate ion is a powerful oxidizing agent, so it is unstable with ions that are easily oxidized.
7. Carbonates (CO$_3^{2-}$), phosphates (PO$_4^{3-}$), oxalates (C$_2$O$_4^{2-}$) and chromates (CrO$_4^{2-}$) tend to be only soluble in acidic solution. An exception is calcium oxalate that is insoluble even in acid. Other exceptions include the salts with cations listed in Rules 2 and 3 (these are soluble in acidic, neutral and basic solution) and magnesium oxalate that is somewhat soluble.
8. Hydroxides (OH$^-$) are insoluble, except for Ba$^{2+}$, Sr$^{2+}$ and the ions listed in Rules 2 and 3. Some metals are soluble in excess hydroxide due to complex ion formation.
9. Thiosulfates (S$_2$O$_3^{2-}$) are soluble, except for Pb$^{2+}$, Ba$^{2+}$ and Ag$^+$.
10. Ferrocyanides [Fe(CN)$_6^{3-}$] are insoluble, except for ions listed in Rules 2 and 3.
Table 4: Some soluble complexes of metal cations

<table>
<thead>
<tr>
<th>Cation</th>
<th>NH₃</th>
<th>OH⁻</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>Ag(NH₃)₂⁺</td>
<td></td>
<td>AgCl⁻</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td></td>
<td>Pb(OH)₄⁻</td>
<td>PbCl₂⁻</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>Cu(NH₃)₄²⁺</td>
<td>Cu(OH)₄⁻</td>
<td>CuCl₄⁻</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td></td>
<td>Cr(OH)₆⁻</td>
<td></td>
</tr>
<tr>
<td>Cr⁶⁺</td>
<td></td>
<td></td>
<td>Cr₂O₇⁻</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>Ni(NH₃)₆²⁺</td>
<td></td>
<td>NiCl₆⁻</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>Zn(NH₃)₄²⁺</td>
<td>Zn(OH)₄⁻</td>
<td></td>
</tr>
<tr>
<td>Al³⁺</td>
<td></td>
<td>Al(OH)₆⁻</td>
<td></td>
</tr>
<tr>
<td>Fe³⁺</td>
<td></td>
<td></td>
<td>FeCl⁻, FeSCN²⁻</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td></td>
<td></td>
<td>MnO₄⁻</td>
</tr>
</tbody>
</table>

Figure 1: Partially completed flowchart for the separation of Groups A through D.

- **snt** = supernatant
- **ppt** = precipitate

```
Ag⁺, Pb²⁺, Mn²⁺, Fe³⁺, Bi³⁺, Al³⁺, Cr³⁺, Ca²⁺, Ba²⁺, Sr²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Mg²⁺

<table>
<thead>
<tr>
<th>snt</th>
<th>6 M HCl</th>
<th>ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>snt</td>
<td></td>
<td>ppt</td>
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<tr>
<td>Add precipitating agent: to be determined later</td>
<td></td>
<td></td>
</tr>
<tr>
<td>snt</td>
<td></td>
<td>ppt</td>
</tr>
</tbody>
</table>
```

Group A

Group B

Group C

Group D

Group B2

Group B1