# A QUALITATIVE ANALYSIS FOR SELECT CATIONS

- To learn about how to develop of a Qualitative Analysis Scheme.
- To learn about Separation of Cations in an Aqueous Solution.
- To learn about Precipitation Equilibria.
- To learn about Complex Ion Formation.

In this laboratory exercise we will separate and identify cations dissolved in an aqueous system. Since we will not quantify the amount of each cation present, but instead merely discern its presence, such a scheme for separation and identification is referred to as a Qualitative Analysis. In our particular case, we will be testing for the presence of the following nine cations:

$$Ag^+, Pb^{2+}, Cu^{2+}, Bi^{3+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, K^+$$
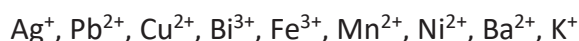
This exercise is useful as a study of aqueous equilibria involving precipitates and complexes, which have important applications in chemistry. The general approach to separating these cations is to group them according to the types of precipitates they form: Chlorides (Cl^-), Sulfides (S^{2-}), Hydroxides (OH^-), etc. We will proceed by selectively precipitating the cations in each Group. Once a Group of cations is precipitated, the cations will be further separated using techniques specific to that Group. Once each cation is separated from the others, a confirmatory test will be used to, as the name implies, confirm the cation is actually present. These confirmatory tests are typically cation specific and run the gamut from the formation of brightly colored complexes to producing distinctly colored flames in a Bunsen burner.

Let's consider an example. Suppose we are testing an aqueous sample for the presence of Pb^{2+}, Hg_2^{2+} and Ca^{2+} ions. (Somehow, we know no other cations are present.) We can start to develop a qualitative scheme by testing samples of each cation for precipitation with Chloride (Cl^-). If we do this, we note chloride precipitates form from Pb^{2+} and Hg_2^{2+} solutions. Thus, the Chloride Group, or Group 1, cations include these two ions. We further note that heating each of these precipitates causes the $PbCl_2$ to re-dissolve. This is because $PbCl_2$ is reasonably soluble in water at high temperatures, but Hg_2Cl_2 is not.
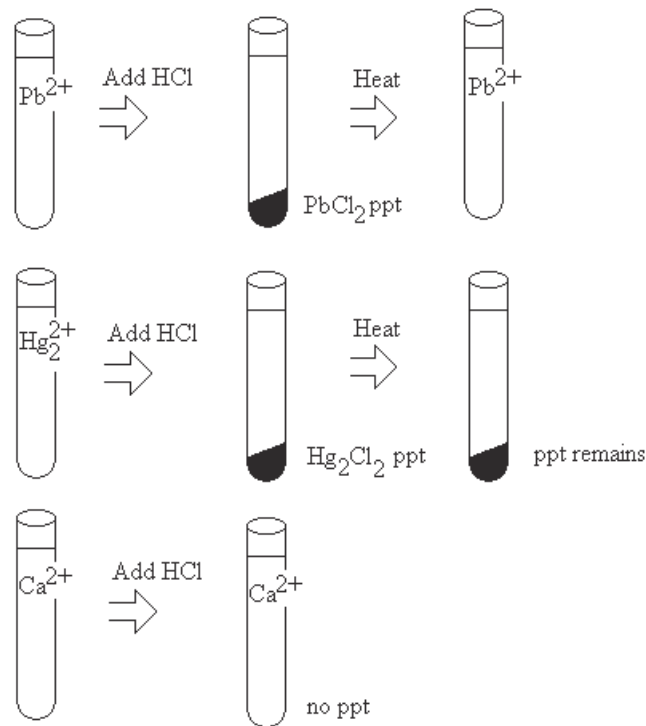
Thus, we have the beginnings of a Qualitative scheme for this cation system; a method for separating them in a mixture. Hydrochloric acid (HCl to) is added to the mixture to precipitate the chloride salts, centrifuge and decant off the supernatant. This separates the Hg_2^{2+} and Pb^{2+} ions from the Ca^{2+} cation. Now, add water to the precipitate and heat. Again, centrifuge and decant off the supernatant. Separation of all the cations is now complete.
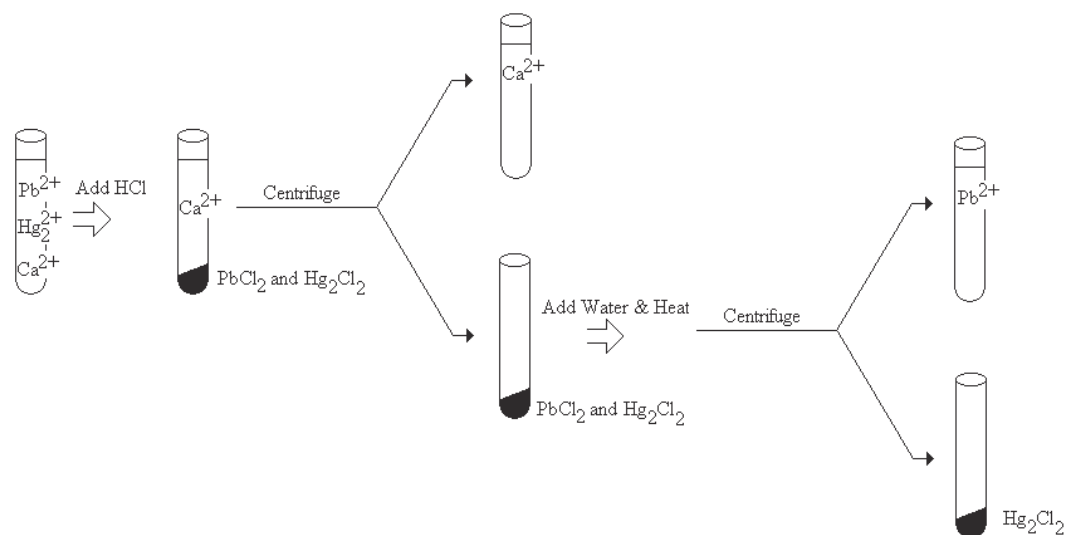
The last piece needed to complete this Qualitative scheme is to add confirmatory tests. After all, how would we ever know the Ca^{2+} was present in our system above; all we see is a clear liquid? And, if you think about it, that clear liquid that we claim contains Pb^{2+} is also just a clear liquid. How do we know Pb^{2+} is actually present? Maybe the only cation present was Hg_2^{2+}? And, it would be nice to know that white chloride precipitate is actually Hg_2Cl_2 and not some other chloride salt. Confirmatory tests are very cation specific. They give a "positive" result when the desired cation is present and a "negative" result if not, or if only other cations are present.

The presence of Pb^{2+} can be confirmed by adding a little Potassium Chromate (K_2CrO_4). The Pb^{2+} precipitates as a golden yellow solid characteristic of $PbCrO_4$. The presence of Hg_2^{2+} is confirmed by adding Aqueous Ammonia, resulting in a dark grey precipitate of $HgNH_2Cl$ and Hg.

The presence of Ca^{2+} must be confirmed by a Flame Test. Many metal cations give off brightly colored light when a few drops are added to a burner flame. Barium gives off green light, Lithium purple and Calcium bright orange. This is because the outer valence electrons are kicked into higher orbitals by the energy of the flame. When the atom relaxes, a photon whose wavelength is dependent on the orbital energy spacing is emitted. Typically a Flame Test is performed by dipping a small loop of nichrome wire into the test solution and placing the drop that hangs on the wire in a Bunsen burner flame. The resulting color is then observed directly.

With these confirmatory tests in hand, we now have a fully developed Qualitative scheme for this system of cations. In Flow chart form, this is represented as:
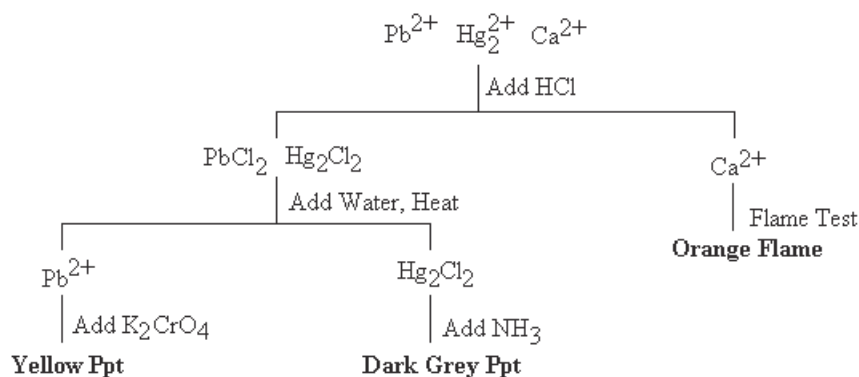
This is the type of scheme you will develop for our list of 9 cations. You will then use this scheme to test a solution of known composition, and one of unknown composition, for the cations present.

How do we know a precipitate will form? Is selective precipitation an effective method of separating cations? How might we re-solubilize our various precipitates so as to run confirmatory tests, etc.?

In order to predict whether or not a precipitate will form, we need to examine the equilibrium between the potential solid and its aqueous ions. Typically, this is written as solubility equilibrium and the equilibrium constant is referred to as a Solubility Product, K_{sp}. For Hg_2^{2+} precipitating as a Chloride (Cl^-) salt, we have:

$$Hg_2Cl_2(aq) \quad \rightleftharpoons \quad Hg_2^{2+}(aq) \quad + \quad 2\,Cl^-(aq)$$
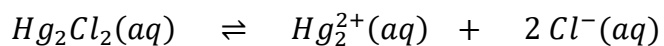
where

$$K_{sp} \quad = \quad [Hg_2^{2+}][Cl^-]^2 \quad = \quad 1 \times 10^{-18}$$

To determine if a precipitate will form, we calculate the reaction quotient, Q, based on the experimental conditions and compare the result with the K_{sp}. There are 2 important outcomes to the relationship between K_{sp} and Q.

If $\quad Q \quad > \quad K_{sp},$ $\qquad$ a precipitate will form

If $\quad Q \quad < \quad K_{sp},$ $\qquad$ a precipitate will not form

Suppose that for a solution mercury (I) chloride Hg_2Cl_2 it is brought to $[Cl^-]$ = 0.1 M by adding HCl and suppose that the concentration of the Hg_2^{2+} ion is also 0.1 M.
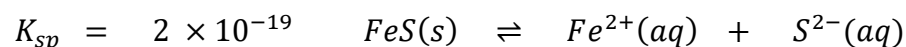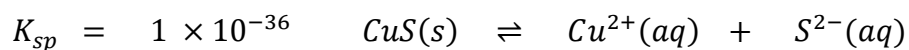
$$Q \quad = \quad [Hg_2^{2+}][Cl^-]^2 \quad = \quad (0.10)(0.10)^2 \quad = \quad 1 \times 10^{-3}$$

$$1 \times 10^{-3} \quad > \quad 1 \times 10^{-18},$$

$$Q \quad > \quad K_{sp,}$$

In this scenario a precipitate will form.

This type of information can be used to selectively precipitate one cation and not another. For example, suppose that there is a solution that contains 0.1 M Cu^{2+} and 0.1 M Fe^{2+}. It is possible to bring the sulfide (S^{2-}) concentration high enough to precipitate 99.999% of the Cu^{2+} without precipitating the Fe^{2+}. The relevant equilibria are

$$K_{sp} \quad = \quad 1 \times 10^{-36} \qquad CuS(s) \quad \rightleftharpoons \quad Cu^{2+}(aq) \quad + \quad S^{2-}(aq)$$

$$K_{sp} \quad = \quad 2 \times 10^{-19} \qquad FeS(s) \quad \rightleftharpoons \quad Fe^{2+}(aq) \quad + \quad S^{2-}(aq)$$

This can be done by first determining the sulfide (S^{2-}) concentration required to precipitate the 99.999% of the Cu^{2+}, in other words 0.001% or 0.00001×0.1 M = 10^{-6} M will remain. With this concentration of Cu^{2+}, the sulfide concentration will be

$$K_{sp} \quad = \quad 1 \times 10^{-36} \quad = \quad [Cu^{2+}][S^{2-}] \quad = \quad (10^{-6})(S^{2-})$$

or,

$$[S^{2-}] \quad = \quad 10^{-30} \ M$$

Thus the reaction quotient, Q, for the FeS system under these conditions will equal

$$Q \quad = \quad [Fe^{2+}][S^{2-}] \quad = \quad (0.1)(10^{-30}) \quad = \quad 10^{-31}$$

Comparing this value with that of the K_{sp} for FeS we see that

$$Q \quad \lll \quad K_{sp}$$

so no FeS will precipitate. In other words, precipitation using the sulfide ion is an effective means of separating Cu^{2+} from Fe^{2+} in an aqueous system.

A final concern is how to re-solubilize, selectively, salts from co-precipitates. One method is to change the pH of the solution. Zinc carbonate ($ZnCO_3$) is an example of a precipitate that re-solubilizes as the pH is lowered by adding acid (H^+) to the system.

$$ZnCO_3(aq) \ + \ 2H^+(aq) \ \rightarrow \ Zn^{2+}(aq) \ + \ H_2CO_3(aq)$$
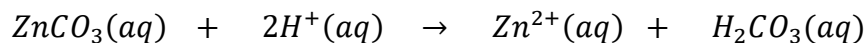
Another trick is to form complex ions of the cation. For example, in an ammonia (NH_3) solution, Ag^+ forms the complex $Ag(NH_3)_2{}^+$

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

$$Ag^+(aq) \ + \ 2NH_3(aq) \ \rightleftharpoons \ Ag(NH_3)_2^+(aq)$$
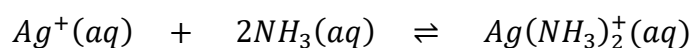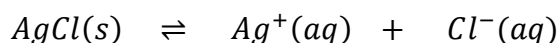
The second of these reactions is referred to as a formation reaction. The complex ion is "formed" from the cation Ag^+ with the ligands of NH_3. The equilibrium constant is known as the formation constant K_f.

The system of 9 cations that will be analyzed will be selectively precipitated into 4 groups.
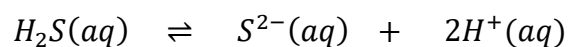
Group I

The cations in this group, Ag^+, Pb^{2+} and Hg_2^{2+}, precipitate as a chloride. Using the mercury (I) cation as an example we have

$$Hg_2^{2+}(aq) \ + \ 2Cl^-(aq) \ \rightarrow \ Hg_2Cl_2(s)$$
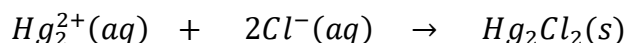
Group II

The cations in this group, Bi^{3+}, Cu^{2+}, Cd^{2+} and Sn^{4+}, do not precipitate as chlorides, but will precipitate upon treatment with hydrogen sulfide (H_2S). In an aqueous environment, hydrogen sulfide dissociates as a weak acid

$$H_2S(aq) \quad \rightleftharpoons \quad S^{2-}(aq) \quad + \quad 2H^+(aq)$$

If the solution is already acidic, the equilibrium will shift to the left and the concentration of S^{2-} will remain fairly low. This will cause that the very insoluble sulfides from this group precipitate. Using the cadmium (II) cation as an example we have
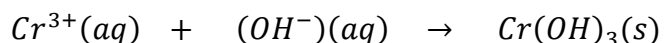
$$Cd^{2+}(aq) \quad + \quad S^{2-}(aq) \quad \rightarrow \quad CdS(s)$$
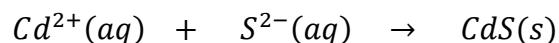
Group III

The cations in this group, Fe^{2+}/Fe^{3+}, Mn^{2+}, Ni^{2+} and Cr^{3+}, precipitate as hydroxides in an ammoniacal solution because of the presence of the hydroxide (OH^-) ion

$$NH_3(aq) \quad + \quad H_2O \quad \rightleftharpoons \quad (OH)^-(aq) \quad + \quad NH_4^+(aq)$$

Using the chromium (III) cation as an example we have

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

Group IV

The cations in this group, K^+, Ca^{2+} and Ba^{2+}, do not precipitate. They will remain in solution even after performing the procedures to precipitate the cations in groups I, II and III.

Pre-Lab Safety Questions

1. Many of the solutions we will be working with contain "Heavy Metals". What does this phrase mean? What are some examples of Heavy Metals? How is ingestion of Heavy Metals treated in Humans?

2. What is the LD_{50} for Hydrosulfide gas? Consult an SDS for Hydrogen Sulfide. What are the effects of inhaling low concentrations of Hydrogen Sulfide?

3. Prepare a Flow Chart indicating how you will separate and confirm the presence of each of the ten Cations in a mixture of these Cations. You will need this Flow Chart in order to complete the second part of the laboratory exercise. You will not be allowed to start the second part of the laboratory without this Flow Chart. Identify potentially "toxic" substances listed on your flow chart.

General Precautions

1. Pb^{2+}, Bi^{3+}, Cu^{2+}, Mn^{2+}, Ni^{2+} and Ba^{2+} salts are toxic. Wash your hands after their use.

2. Ag^+ will stain your skin.

3. CrO_4^- is toxic and will burn your skin.

4. Thioacetamide is toxic and produces toxic H_2S gas.

5. HNO_3, H_2SO_4 and HCl are acids and will burn your skin

<u>Beginning the Experiment</u>

1. Obtain a "known" mixture of cations. Perform your analysis on this sample. Identify the cations in this mixture. Confirm your results with your laboratory instructor. Repeat any tests that are not consistent with the "known" results.

2. Obtain an "unknown" mixture of cations. Perform your analysis on this sample.

<u>Precipitation of Group I Cations</u>

1. Measure 15 drops of the Known (or Unknown) Mix of cations solution into a test tube. This mixture contains all (or at least 2 in the case of the Unknown) of the experimental cations (Ag^+, Pb^{2+}, Bi^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, K^+) to be analyzed. Dilute the sample with the same amount of drops of deionized water. Add 10 drops of 6 M HCl, stir thoroughly, and then centrifuge for 2 minutes. Group I cations form a chloride precipitate.

$$X^{n+}(aq) \quad + \quad nCl^- \quad \rightarrow \quad XCl_n(s)$$
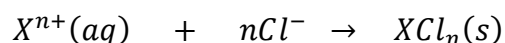
2. Separate the liquid part (supernatant) to a different clean test tube and set it aside for the *<u>Precipitation of Group II Cations</u>* analysis. Label this and all tubes used appropriately to avoid confusion and misuse. Failure to do this may lead to a very confusing and time consuming experience.

3. Wash the remaining solid (precipitate) in the test tube by adding 10 drops of cold deionized water and stir the mixture thoroughly. Centrifuge the mixture for 2 minutes. Discard the resulting supernatant.

4. Add 20 drops of deionized water to the solid in the test tube and place it in a hot-water bath. Stir the sample with your stirring rod for about a minute and the quickly remove it from the hot water bath and centrifuge it for 2 minutes. Pour the supernatant (liquid part) into a clean test tube and label it so it can be used for the confirmation of lead (II). Save the solid that did not dissolve. At this point you should have 2 test tubes; one with the supernatant you saved which contains Pb^{2+}, and one with the solid that remained which is AgCl.
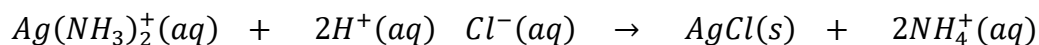
5. <u>Confirmation for the Presence of Pb^{2+}</u>

Take the test tube that you labeled for the use of confirmation of lead (II) (the one with supernatant you saved) and add 3 drops of 1 M K_2CrO_4. The formation of a yellow precipitate, $PbCrO_4$, indicates the presence of the lead (II) ion in your sample.

$$Pb^{2+}(aq) \quad + \quad CrO_4^{2-}(aq) \quad \rightarrow \quad PbCrO_4(s)$$
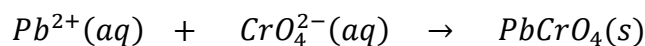
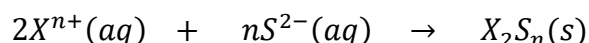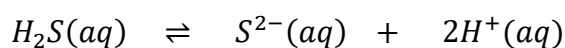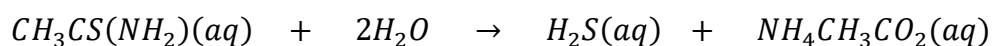6. <u>Confirmation for the Presence of Ag^+:</u>

Add 6 drops of 6 M $NH_3(aq)$ (labeled as 6 M NH_4OH) to the solid sample (AgCl) in the other test tube and mix it thoroughly. Centrifuge and decant the supernatant into a clean test tube. To this liquid (decantate) add 20 drops of 6 M HNO_3. Mix the solution and test it for acidity using blue litmus paper. If the sample is acidic the paper will turn pink. Continue to add 6 M HNO_3 until the litmus paper turns pink. The appearance of a white cloudiness confirms the presence of Ag^+.

$$AgCl(s) \quad + \quad 2NH_3(aq) \quad \rightarrow \quad Ag(NH_3)_2^+(aq) \quad + \quad Cl^-(aq)$$

$$Ag(NH_3)_2^+(aq) \quad + \quad 2H^+(aq) \quad Cl^-(aq) \quad \rightarrow \quad AgCl(s) \quad + \quad 2NH_4^+(aq)$$

The lead (II) cation was confirmed by the presence of the yellow precipitate of $PbCrO_4$ and the silver (I) cation was confirmed by reprecipitation of the white precipitate of AgCl.

Precipitation of Group II Cations

1. In a fume hood, add 25 drops of 1 M thioacetamide to the supernatant that you separated and saved in the *Precipitation of Group I Cations* part. This decantate contains the cations for Group II (Bi^{3+} and Cu^{2+}), Group III (Fe^{2+}, Mn^{2+}, and Ni^{2+}) and Group IV (Ba^{2+} and K^+). Continuing to work in the fume hood, heat the sample in a hot water bath for 10 minutes. This allows the thioacetamide to decompose into hydrogen sulfide (H_2S) and allows the sulfide precipitates to form in an acidic environment.

$$CH_3CS(NH_2)(aq) \quad + \quad 2H_2O \quad \rightarrow \quad H_2S(aq) \quad + \quad NH_4CH_3CO_2(aq)$$

$$H_2S(aq) \quad \rightleftharpoons \quad S^{2-}(aq) \quad + \quad 2H^+(aq)$$

$$2X^{n+}(aq) \quad + \quad nS^{2-}(aq) \quad \rightarrow \quad X_2S_n(s)$$

    During the 10-minute interval use a glass rod to mix the sample periodically. Centrifuge the resulting mixture for 5 minutes and afterwards decant the supernatant into a clean test tube and save the precipitate and label appropriately. The solid (precipitate) will be used for the confirmation of bismuth (III) and copper (II). The tube with the supernatant (liquid) will be used for the *Precipitation of Group III Cations*.

2. Take the precipitate that you separated for the confirmation of Bi^{3+} and Cu^{2+}, and in a fume hood, add 10 drops of 6 M HNO_3 to it, and heat it in a hot water bath until the precipitate dissolves. A light-colored residue of sulfur may remain. Ignore it. It will not affect the analysis. Dissolution of the precipitate is the result of the H^+ combining with the sulfide (S^{2-}) to reform the H_2S. If the mentioned residue remains, centrifuge your mixture and transfer the supernatant in to a clean test tube using a clean transfer pipet. You can discard the residue.

$$X_2S_n(s) \quad + \quad 2nH^+(aq) \quad \rightarrow \quad 2X^{n+}(aq) \quad + \quad nH_2S(aq)$$
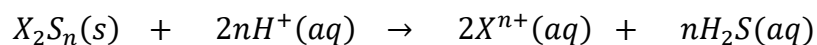
3. Confirmation for the Presence of Cu^{2+}

Take the tube with the supernatant and, in the fume hood, add 15 M NH$_3$(aq) drop wise until it turns red litmus paper blue. This indicates that the solution is basic. Add 3 more drops of 15 M NH$_3$(aq). A deep blue color confirms the presence of the copper (II) ion. A white gelatinous precipitate will also appear. Centrifuge the mixture and separate the blue supernatant in to a clean test tube. The white precipitate is used for the confirmation of the presence of Bi^{3+}.

$$Cu^{2+}(aq) \ + \ 4NH_3(aq) \ \rightarrow \ Cu(NH_3)_4^{2+}(aq)$$
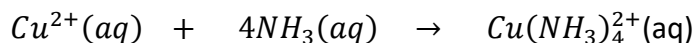
4. Confirmation for the Presence of Bi^{3+}

The white gelatinous precipitate that was saved from the previous step indicates the presence of the bismuth (III) ion.

$$Bi^{3+}(aq) \ + \ 3NH_3(aq) \ + \ 3H_2O \ \rightarrow \ Bi(OH)_3(s) \ + \ 3NH_4^+(aq)$$
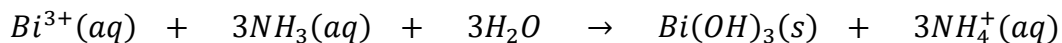
The presence of the bismuth (III) cation can be further confirmed by additional chemistry. Add 10 drops of hot deionized water to the precipitate, mix the sample and centrifuge for 2 minutes. Discard the supernatant. Add 6 drops of 6 M NaOH and 4 drops of freshly prepared 0.2 M SnCl$_2$ to the precipitate and mix thoroughly. The formation of a jet-black precipitate conforms the presence of the bismuth (III) ion.

$$2Bi(OH)_3(aq) \ + \ 3Sn(OH)_4^{2-}(aq) \ \rightarrow \ 2Bi(s) \ + \ 3Sn(OH)_6^{2-}(aq)$$
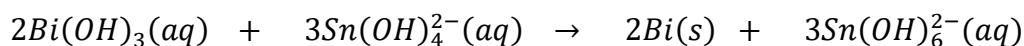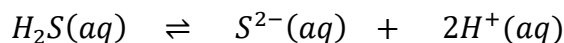
Precipitation of Group III Cations

1. Working in a fume hood, take the decantate (liquid) that you saved for this part and add 15 M $NH_3(aq)$ drop wise until the solution turns red litmus paper blue. Add an additional 2 drops of the concentrated ammonia (15 M $NH_3(aq)$). The ammonia makes the solution basic.

$$NH_3(aq) \quad + \quad H_2O \quad \rightleftharpoons \quad (OH)^-(aq) \quad + \quad NH_4^+(aq)$$
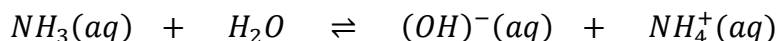
This does two things. It allows the precipitation of the *Group III* cations as hydroxides, and

$$X^{n+}(aq) \quad + \quad n(OH)^- \quad \rightarrow \quad X(OH)_n(s)$$
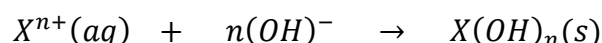
it consumes the H^+ ions, causing the H_2S equilibrium to shift to the right as predicted by Le Chatelier's Principle, dramatically increasing the concentration of the sulfide (S^{2-}) ion.

$$H_2S(aq) \quad \rightleftharpoons \quad S^{2-}(aq) \quad + \quad 2H^+(aq)$$

This allows for *Group III* cations that form slightly soluble sulfides to precipitate.

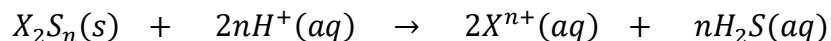$$2X^{n+}(aq) \quad + \quad nS^{2-}(aq) \quad \rightarrow \quad X_2S_n(s)$$
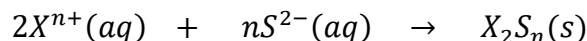
If a precipitate forms, test for complete precipitation by centrifuging the sample and in a fume hood add an additional drop of 15 M $NH_3(aq)$. If a precipitate formed, mix the sample thoroughly, centrifuge and repeat until no precipitate is formed when you add the extra drop of concentrated ammonia. Separate the supernatant (liquid) into a clean test tube and label it appropriately. This solution will be used for the *Precipitation of Group IV Cations*.

2. Take the precipitate contained in your test tube, and in the fume hood, add 3 drops of 16 M HNO_3 and 9 drops of 12 M HCl. Warm the sample in a hot tap water bath until the precipitate dissolves. The hydroxides dissolve due to the presence of the H^+.

$$X(OH)_n(aq) \quad + \quad nH^+(aq) \quad \rightarrow \quad X^{n+}(aq) \quad + \quad nH_2O$$
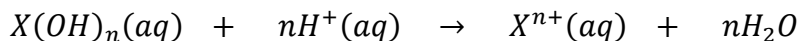
The sulfides dissolve as before.

$$X_2S_n(s) \quad + \quad 2nH^+(aq) \quad \rightarrow \quad 2X^{n+}(aq) \quad + \quad nH_2S(aq)$$

The nitric acid (HNO_3) oxidizes the hydrogen sulfide (H_2S) to keep the sulfide precipitate from forming. Centrifuge the solution for 2 minutes and transfer the supernatant (liquid) in to a clean test tube. This is done to remove any sulfur that might have formed.

3. Take the supernatant and add 6 M NaOH until the solution is strongly basic. Red litmus paper will turn blue when it is. This allows the cations to re-precipitate as hydroxides.

$$X^{n+}(aq) \quad + \quad n(OH)^- \quad \rightarrow \quad X(OH)_n(s)$$
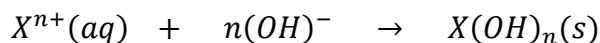
If the precipitate is pasty, add 12 drops of deionized water. Centrifuge the mixture and discard the supernatant. Add 20 drops of deionized water and 10 drops of 6 M H_2SO_4 to the remaining solid. Mix thoroughly and place in a hot water bath for at least 3 minutes or until the precipitate dissolves. If the precipitate does not dissolve after 5 minutes, remove the sample from the water bath add 12 drops of deionized water, mix the sample thoroughly and centrifuge for couple of minutes. Transfer the supernatant equally in to 3 different clean test tubes. If the sample does dissolve just add 12 drops of deionized water, mix thoroughly and transfer the solution equally in to 3 different clean test tubes.
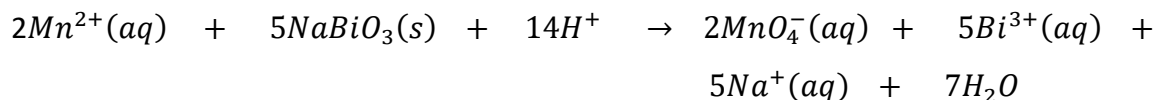
4. <u>Confirmation for the Presence of Fe^{3+}</u>

    Take one of the 3 test tubes you made and add 2 drops of 0.2 M KSCN. The appearance of a brick red color indicates the presence of the iron (III) cation. The color is the result of the complex formed between the iron (III) and the thiocyanate ions.
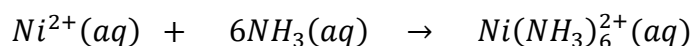
$$Fe^{3+}(aq) \quad + \quad SCN^-(aq) \quad \rightarrow \quad Fe(SCN)^{2+}(aq)$$
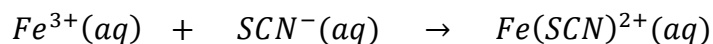
<u>Confirmation for the Presence of Mn^{2+}</u>

Take another of the 3 test tubes you made and add 4 drops of 3 M HNO$_3$ and 4 drops of deionized water. Mix the sample thoroughly and add a few grains of sodium bismuthate (NaBIO$_3$). Mix the sample thoroughly and centrifuge it for a couple of minutes. The appearance of a pink or purple color solution indicates the presence of manganese (II) ion. The color is due to the presence of the permanganate anion (MnO_4^-).

$$2Mn^{2+}(aq) \; + \; 5NaBiO_3(s) \; + \; 14H^+ \; \rightarrow \; 2MnO_4^-(aq) \; + \; 5Bi^{3+}(aq) \; + \; 5Na^+(aq) \; + \; 7H_2O$$

5. <u>Confirmation for the Presence of Ni^{2+}</u>

Take the last test tube of the 3 test tubes you made and add 6 M NH$_3$(aq) until the solution is basic to litmus red paper. Once the solution is basic, add 4 drops of dimethylglyoxime (DMG). The appearance of a red precipitate indicates the presence of the nickel (II) ion. The DMG complexes with the nickel (II) to form the intense red precipitate.

$$Ni^{2+}(aq) \; + \; 6NH_3(aq) \; \rightarrow \; Ni(NH_3)_6^{2+}(aq)$$

$$Ni(NH_3)_6^{2+}(aq) \; + \; 2H_2DMG(aq) \; \rightarrow \; Ni(HDMG)_2(s) \; + \; 4NH_3(aq) \; + \; 2NH_4^+(aq)$$

At this point iron (III), manganese (II) and nickel (II) have been confirmed.

Precipitation of Group IV Cations

As mentioned previously, the cations in this group do not form precipitates as the cations in groups II, III and IV. A traditional method for these cations is the use of the flame test. Many metal cations give off brightly colored light when a few drops are added to a burner flame. Barium gives off a green light, calcium a bright orange and potassium a purple flame. This is because the outer valence electrons are kicked into higher orbitals by the energy of the flame. When the atom relaxes, a photon whose wavelength is dependent on the orbital spacing energy spacing is emitted. Typically, a flame test is performed by dipping a small loop of nichrome wire into the test solution and placing the drop that hangs on the wire in a Bunsen burner flame. The

resulting color is observed directly. Because flame test are concentration dependent, they cations are sometimes hard to observe if the concentration is too small. To facilitate the confirmation of the 2 cations (Ba²⁺, K⁺) that are being analyzed, a different approach will be used for each.

1. Confirmation for the Presence of Ba²⁺

Split the decantate that was saved for *Precipitation of Group IV Cations* in to 2 clean test tubes. Take one of the tubes and add 8 drops of 6 M acetic acid (CH_3COOH) and 1 drop of 1 M K_2CrO_4. A yellow precipitate indicates the presence of Ba²⁺.

$$Ba^{2+}(aq) \ + \ CrO_4^{2-}(aq) \ \rightarrow \ BaCrO_4(s)$$
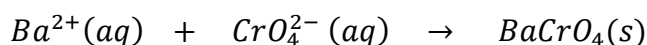
2. Confirmation for the Presence of K⁺

Take the other tube and add 6 drops of 1 M NaOH. This is done to make the solution basic and to help eliminate the NH_4^+ present in the solution because it interferes with the test for K⁺. Gently boil the solution to help expel the any NH_3. Then acidify with 2 drops of 6 M HCl and 15 drops of 1 M sodium acetate ($NaCH_3COO$). The acetate ions react with excess H⁺ and buffer the solution at about pH 5. Add 3 drops of 3% sodium tetraphenylborate, $NaB(C_6H_5)_4$. A white precipitate of potassium tetraphenylborate $KB(C_6H_5)_4$ indicates the presence of the potassium ion.

$$K^+(aq) \ + \ NaB(C_6H_5)_4(aq) \ \rightarrow \ KB(C_6H_5)_4(s) \ + \ Na^+(aq)$$