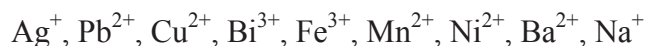


A Qualitative Analysis for Select Cations

- To learn about how to Develop 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.
- To learn about Flame Tests for Cations.

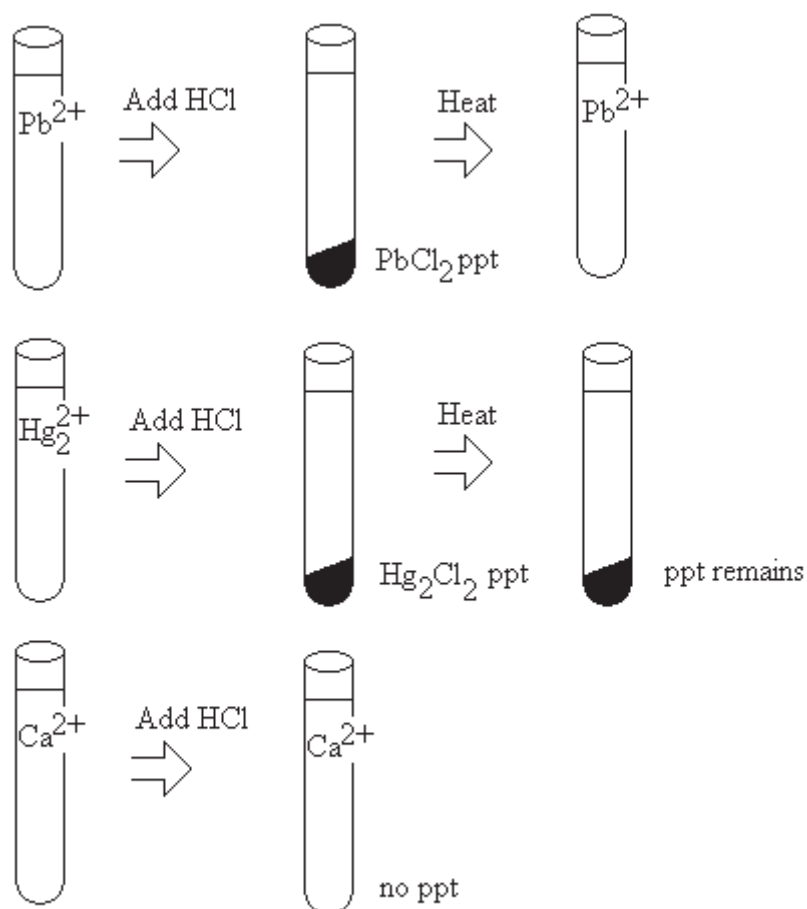
In this laboratory exercise we will separate and identify Cations dissolved in an Aqueous system. Since we will not quantify the amount of each Cation present, but instead merely discern its presence, such a scheme for separation and identification is referred to as a Qualitative Analysis. In our particular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



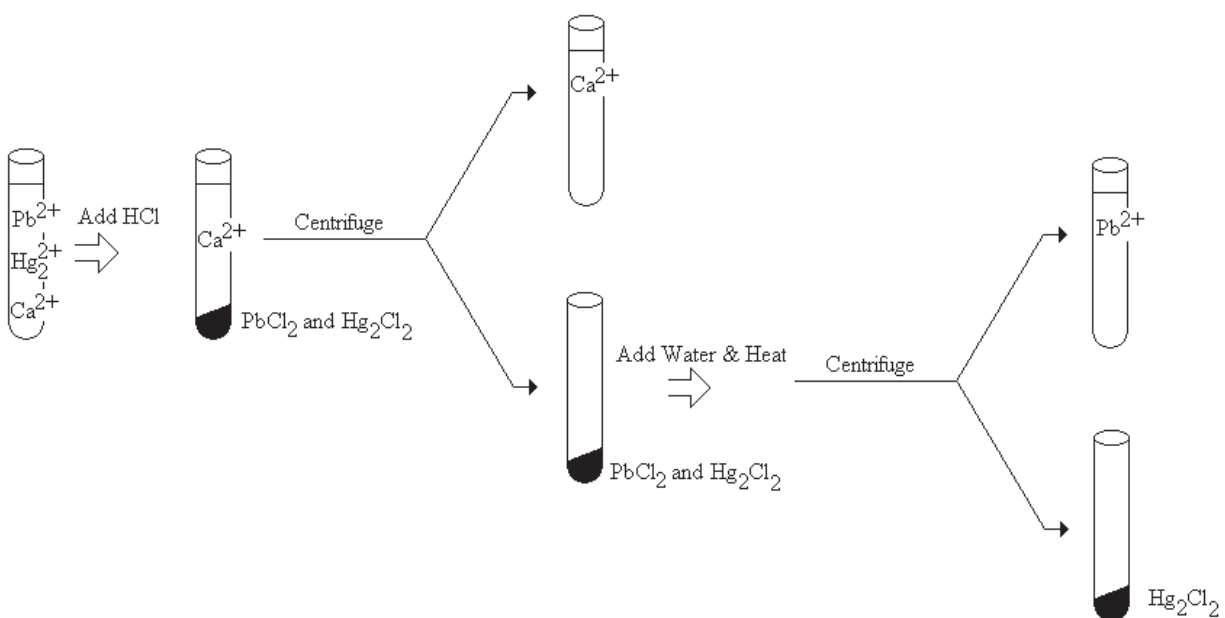
Although this style of “wet chemical” analysis is no longer commonly used to determine the presence of these Cations, the development of this type of Qual scheme has many other applications in chemistry. Additionally, this exercise is useful as a study of Aqueous equilibria involving precipitates and complexes, each of which do have important applications in chemistry.

Our 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 Qual scheme by testing separate 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 Qual scheme for this Cation system; a method for separating these Cations in a mixture of these Cations. To the mixture of Cations, add HCl 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+} . Now, add Water to the precipitate and heat. Again, centrifuge and



decant off the supernatant. Separation of all the Cations is now complete.

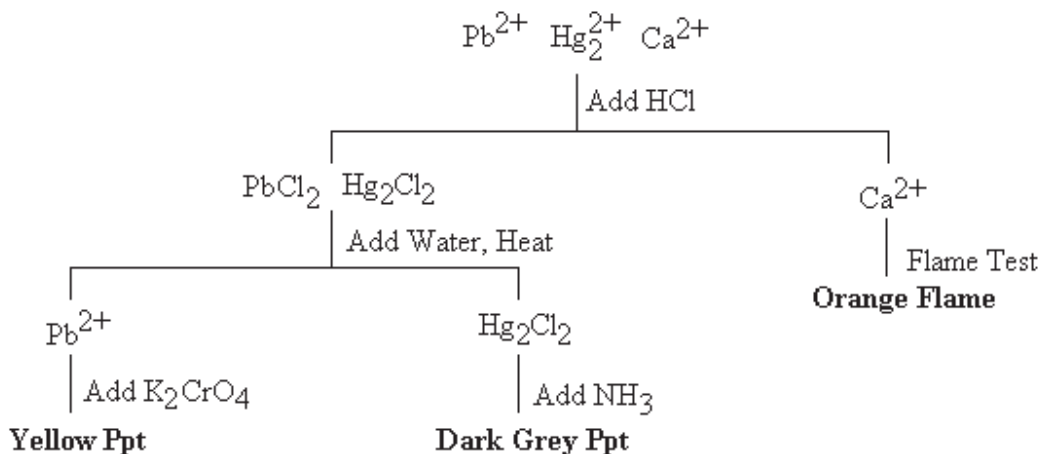
The last piece needed to complete this Qual scheme is to add confirmatory tests. After all, how would we ever know the Ca^{2+} was present in our system above; all we see is a clear liquid. And, if you think about it, that clear liquid that we claim contains Pb^{2+} is also just a clear liquid. How do 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. Ba gives off green light, Li purple and Ca 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 Nicrome 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 Qual 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.

Now, to some of those pesky details. 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 a 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:



where:

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

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} . If:

$$Q > K_{sp} \quad \text{A ppt will form} \quad (Eq. 3)$$

and if:

$$Q < K_{sp} \quad \text{A ppt will not form} \quad (Eq. 4)$$

For our Mercurous Chloride (Hg_2Cl_2) example, suppose our mixture is brought to $[Cl^-] = 0.1M$ by adding HCl. Further suppose the Hg_2^{2+} Cation is at 0.1M. We have:

$$Q = [Hg_2^{2+}][Cl^-]^2 = (0.10)(0.10)^2 = 10^{-3}$$

So,

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

and a precipitate will form.

Next, we desire to know if precipitation can be used to selectively precipitate one Cation and not another. For instance, suppose we have a solution containing Cu^{2+} and Fe^{2+} , both at 0.1M. Is it possible to bring the Sulfide (S^{2-}) concentration high enough to precipitate 99.999% of the Cu^{2+} without also precipitating the Fe^{2+} . The relevant equilibria are:



First, determine the Sulfide concentration needed to precipitate 99.999% of the Cu^{2+} ; meaning 0.001%, or $0.00001 \times 0.1\text{M} = 10^{-6}\text{M}$, will remain. At this point, using the Equilibrium Constant Expression, we have a Sulfide Ion concentration of:

$$K_{\text{sp}} = 1 \times 10^{-36} = [\text{Cu}^{2+}] [\text{S}^{2-}] = (10^{-6}) [\text{S}^{2-}] \quad (\text{Eq. 7})$$

or,

$$[\text{S}^{2-}] = 10^{-30} \text{ M} \quad (\text{Eq. 8})$$

Thus, the Reaction Quotient, Q, for the FeS system under these conditions will equal:

$$Q = [\text{Fe}^{2+}] [\text{S}^{2-}] = (0.1) (10^{-30}) = 10^{-31} \quad (\text{Eq. 9})$$

Comparing this with the K_{sp} for FeS, we see:

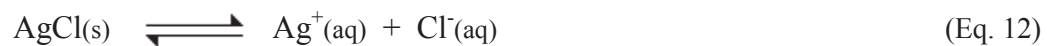
$$Q \lll K_{\text{sp}} \quad (\text{Eq. 10})$$

So, no FeS will precipitate. In other words, precipitation using 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 that form co-precipitates. One method is to change the pH of the solution. Zinc Carbonate is an example of a precipitate that re-solubilizes as the pH is lowered by adding Acid (H^+) to the system:



Another trick is to form complex ions of the Cation. For example, in an Ammonia (NH_3) solution, Ag^+ , forms an $\text{Ag}(\text{NH}_3)_2^+$ complex:



The second of these reactions is referred to as a Formation Reaction, the complex ion is “formed” from the Cation (Ag^+) and its ligands (NH_3), and the Equilibrium Constant is a Formation Constant, K_{f} .

For our system of 9 Cations, we will selectively precipitate them in four Groups. These are:

Group 1

Group 1 Cations precipitate as a Chloride. From the examples above, we note Hg_2^{2+} (not a Cation in our system) is a Group 1 Cation:



Group 2

Group 2 Cations 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:

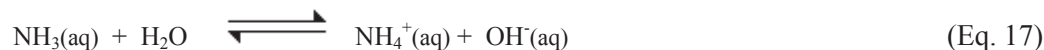


If the solution is already Acidic, the equilibrium will shift left and the concentration of S^{2-} will remain fairly low. Thus, only very insoluble Sulfides will precipitate in this Group. Cd^{2+} , another example not in our system, is a member of this Group:

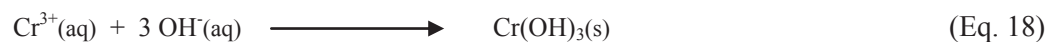


Group 3

These Cations precipitate in an Ammoniacal Solution. Because Ammonia solutions are Basic (OH^-):



many of the Cations in this Group precipitate as Hydroxides. Cr^{3+} is an example:



Other members of this Group precipitate as the Sulfide. This is because the Basic environment causes the Hydrogen Sulfide equilibrium to shift toward the Right:



drastically increasing the Sulfide Ion (S^{2-}) concentration. This causes Sulfides that are otherwise more soluble (*i.e.*, did not precipitate as a Group 2 Cation.) to suddenly precipitate.

Group 4

These are Cations that do not precipitate. They will remain in solution even after performing the procedures to precipitate the Group 1, 2, and 3 Cations.

Thus, we will initially treat all 9 of our Cations individually with the Group 1 precipitating reagent (HCl) to determine which are members of this Group. Once this is determined, we will then examine methods for separating them and confirming their presence. Having completed this task, we will proceed with the remaining Cations and categorize, separate and confirm them. Once this has been completed with the individual Cations, a Qual Scheme for these Cations will be constructed. And, having done this, we will proceed to the task of analyzing a mixture of these possible Cations of unknown composition.

Pre-Lab Safety Questions

Week 1

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 LD₅₀ for Hydrosulfide gas? Consult an SDS for Hydrogen Sulfide. What are the effects of inhaling low concentrations of Hydrogen Sulfide?

Week 2

1. 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.

Procedure

During Week 1 you will test the precipitation and confirmation reactions for each Cation individually. Thus, you will be starting with 9 different samples; each sample containing a single Cation. The procedural steps below are written for this style of testing. You will first identify the Cations in a given Group, and then move on to separating and confirming their presence. Once you identify each Group of Cations, it is important to run the confirmatory tests on all the Cations in that Group. This is necessary because you need to show the test confirms the presence of the target Cation and is negative for other Cations. As you move through these procedural steps, you should begin to build a flow chart for how the Cations can be separated from a mixture.

During Week 2 you will follow your flow chart for the separation and identification of Cations in a mixture. You will do this for two mixtures; a mixture of known Cation composition and a mixture of unknown composition. It is important that you realize some of the procedural steps may need to be modified because you will have only a single sample containing the various Cations and not, as is the case during Week 1's analysis, many samples containing a single Cation.

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^{2-} 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.

Week 1

Confirmation for the Presence of Na^{+}

Because Na^{+} salts are generally soluble, forming a precipitate of this Cation is difficult. Additionally, Na^{+} selective confirmatory reagents are also difficult to come by. Therefore we will confirm the presence of Na^{+} using a Flame Test. Sodium (Na) will impart a bright yellow color to a flame. Since almost all solutions have traces of Na^{+} present, you must decide if the

yellow Flame color is due to the presence of Na^+ in the original solution, before contaminating reagents are added, or due to contamination imparted during the Qual Scheme. This will be done on the basis of the intensity of the color.

- Using a clean Nicrome Wire loop, perform a Flame Test on each of the original Cation solutions. Also, for comparison, run a flame test on distilled Water and 0.2M NaCl.

Precipitation of Group 1 Cations

- Measure out 10 drops of each of the known Cation solutions. Add 4 drops 6M HCl, stir thoroughly, and then centrifuge. Test for completeness of precipitation by adding 1 drop 6M HCl. If the supernatant is cloudy, stir the solution, add another 2 drops of 6M HCl and repeat the centrifugation and completeness of precipitation steps. Continue this process until the supernatant remains clear. The Group 1 Cations will form a Chloride precipitate.

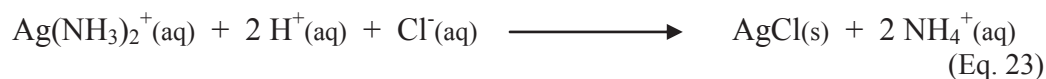


- If the Cation did not produce a precipitate, set it aside for the *Precipitation of Group 2 Cations* analysis.
- If a precipitate did form, discard the supernatant.
- Wash each solid by adding 5 drops of Cold Water and stirring. Centrifuge and discard the supernatant.
- Add 15 drops of Water to each of the solids and place the test tubes into a hot-water bath. Stir using a stir rod for ~ 1 minute. Quickly Centrifuge the hot solution, pour the supernatant into a clean test tube. Repeat this procedure two more times. Retain those solids that do not dissolve.
- Confirmation for the Presence of Pb^{2+} : Add 3 drops of 1M K_2CrO_4 to the supernatant containing Pb^{2+} . PbCrO_4 , a yellow precipitate, should form; confirming the presence of Pb^{2+} .



- Confirmation for the Presence of Ag^+ : To the AgCl precipitate from *Step 5* that did not dissolve in Hot Water, add 6 drops of 6M NH_3 . Centrifuge and decant each supernatant into a clean test tube. Add 20 drops of 6M HNO_3 to the decantate. Stir the solution and test its acidity with litmus. Continue to add HNO_3 until the solution is acidic. A white cloudiness confirms the presence of Ag^+ .

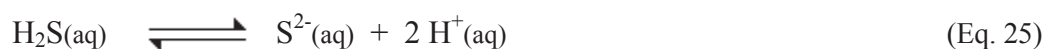




At this point you should have confirmed the presence of the Pb^{2+} and Ag^+ ions.

Precipitation of Group 2 Cations

1. **In the fume hood**, add 10 drops of 1M Thioacetamide ($\text{CH}_3\text{CS}(\text{NH}_2)$) to each of the solutions from the *Precipitation of Group 1 Cations* that did not form a precipitate in *Step 1* of that procedure. **In the fume hood**, heat each solution in a Hot Water bath for 10 minutes. This should allow the Thioacetamide to decompose into Hydrogen Sulfide (H_2S) and allow the Sulfide precipitates to form in an Acidic environment.



If the Cation did produce a precipitate, Centrifuge the solution and decant the supernatant into a clean test tube. Save the precipitate and keep track of which supernatant belongs to which precipitate because if precipitation is not complete, the additional precipitate collected from the supernatant will have to be combined with the initial precipitate. Test the supernatant for completeness of precipitation by, **again in the fume hood**, adding 2 drops of Thioacetamide and allowing it to stand for 1 minute. If more precipitate forms, add a few more drops of Thioacetamide and heat it in a Hot Water bath for 5 minutes. Centrifuge and decant the supernatant. Combine this additional precipitate with that initially formed for each appropriate Cation. Do this by adding 1 drop 0.2M NH_4NO_3 solution and 9 drops Water to the second precipitate, mixing and transferring to the first precipitate. Mix thoroughly, centrifuge and discard the supernatant. Do this for each Cation that produces an additional precipitate.

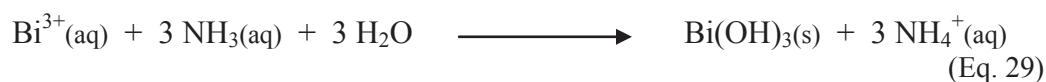
2. If the Cation did not produce a precipitate, keep it for the *Precipitation of Group 3 Cations* analysis.
3. Now, **in a fume hood**, add 10 drops of 6M HNO_3 to each precipitate and heat in a Hot Water bath until the precipitate dissolves. (A light-colored residue of Sulfur may remain.) If the precipitate has not dissolved in 5 minutes, gently heat over a low flame. Centrifuge the solution to remove any Sulfur that forms. Dissolution of the precipitate is the result of H^+ combining with Sulfide (S^{2-}) to reform H_2S .



5. Separation of Bi³⁺ and Confirmation for the Presence of Bi³⁺ and Cu²⁺: **In a fume hood**, add dropwise 15M NH₃ until each solution is basic to litmus and add 3 more drops. A deep blue color confirms the presence of Cu²⁺.



A white gelatinous precipitate indicates Bi³⁺ is present.



This can be confirmed by centrifuging the gelatinous mixture and discarding the supernatant. Wash the precipitate once with 10 drops of Hot Water. Discard the washings. Add 6 drops of 6M NaOH and 4 drops of freshly prepared 0.2M SnCl₂ to the precipitate and stir. The formation of a jet-black precipitate confirms the presence of Bi³⁺.



At this point you should have confirmed the presence of the Cu²⁺ and Bi³⁺ ions.

Precipitation of Group 3 Cations

1. Add 2 drops 2M NH₄NO₃ to each of the solutions from the *Precipitation of Group 2 Cations* that did not form a precipitate in *Step 1* of that procedure. Stir. **In a fume hood**, add dropwise 15M NH₃ until each solution is basic to litmus and add 2 more drops. The Ammonia produces a Basic (OH⁻) solution.



This does two things. It will allow for the precipitation of Group 3 Cations as Hydroxides.



It also consumes H⁺ ions, causing the H₂S equilibrium, by Le Chatelier's Principle, to shift Right, dramatically increasing the concentration of S²⁻ ion.



This means Group 3 Cations that form slightly soluble Sulfides will now precipitate.



If a precipitate forms, test for completeness of precipitation by Centrifuging the sample and, **in a fume hood**, adding an additional drop of 15M NH₃.

- If the Cation did not produce a precipitate, keep it for the *Analysis of Group 4 Cations*.
- In a fume hood**, treat each precipitate with 3 drops 16M HNO₃ and 9 drops 12M HCl. Warm in a Hot Water bath until the precipitate dissolves. The Hydroxides dissolve because of combination with the Acid.



The Sulfides dissolve as before.

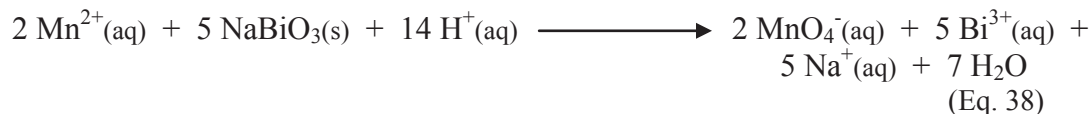


The Nitric Acid (HNO₃) oxidizes the Hydrogen Sulfide (H₂S) to keep the Sulfide precipitate from reforming. Centrifuge the solution to remove any Sulfur that forms.

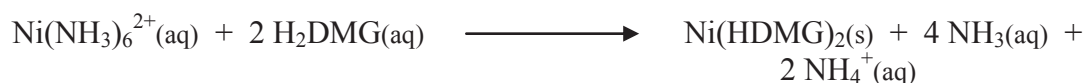
- Re-precipitate the Cations of this Group as Hydroxides by adding 6M NaOH until the solution is strongly Basic. If the precipitate is pasty, add 12 drops of Water. Centrifuge and decant. To each precipitate add 20 drops of Water and 10 drops of 6M H₂SO₄. Stir and heat in the Hot Water bath for 3 minutes or until the precipitate dissolves. Add 12 drops of Water and divide each solution into three parts.
- Confirmation for the Presence of Fe³⁺, Mn²⁺ and Ni²⁺: To the first part for each, add 2 drops 0.2M KSCN. A brick red color indicates the presence of Fe³⁺ because Ferric Thiocyanate has formed (Fe(SCN)²⁺).



To the second part, add a solution prepared from 4 drops 3M HNO₃ and 4 drops Water. Mix and add a few grains of Sodium Bismuthate (NaBiO₃). Mix thoroughly and Centrifuge. A pink or purple color is due to the formation of MnO₄⁻ and indicates the presence of Mn²⁺ originally.



To the third part, add 6M NH₃ until the solution is Basic to litmus. Add about 4 drops of Dimethylglyoxime (DMG). Allow the solution to stand. The DMG complexes with Ni²⁺ to form a pink precipitate.



(Eq. 40)

At this point you should have confirmed the presence of the Fe^{2+} , Mn^{2+} and Ni^{2+} ions.

Analysis of Group 4 Cations

1. Confirmation for the Presence of Ba^{2+} : To each of the remaining solutions, add 8 drops of 6M Acetic Acid ($\text{CH}_3\text{CO}_2\text{H}$) and 1 drop of 1M K_2CrO_4 . A yellow precipitate indicates the presence of Ba^{2+} .



2. Confirmation for the Presence of Na^+ : This was done as a Flame Test on the original sample.

At this point you should have confirmed the presence of the Ba^{2+} and Na^+ ions.

At this point you should have a complete Flow Chart for the separation and confirmation of the presence of any of our 9 Cations.

Week 2

During this week's lab you will follow your flow chart for the separation and identification of Cations in a mixture. You will do this for two mixtures; a mixture of "known" Cation composition and a mixture of unknown composition. It is important that you realize some of the procedural steps may need to be modified because you will have only a single sample containing the various Cations and not, as is the case during Week 1's analysis, many samples containing a single Cation.

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. Re-do any tests that are not consistent with the "known" results.
2. Obtain an "unknown" mixture of cations. Perform your analysis on this sample.

Data Analysis

1. Identify the cations in the “unknown” mixture.