

Separation and Qualitative Determination of Cations and Anions

Introduction

Much of laboratory chemistry is focused on the question of how much of a given substance is contained in a sample. Sometimes, however, the focus shifts to what substances are in the sample, rather than their quantity. In this experiment, an analysis scheme for identifying both cations and anions in solution will be used in determining the ions present in unknown solutions

Concepts

* qualitative analysis

* precipitation reactions

Background

Qualitative analysis is an analytical procedure in which the question "what is present?" is answered. In a systematic qualitative analysis scheme, each substance present is separated from the other substances. Then a confirmatory test is used to prove that the isolated substance is the expected one.

Two solutions, one containing any combination of four different cations, and another containing any combination of four anions will be assigned to each student group. The two "unknown" solutions are then analyzed to determine which ions are present and which are absent. This experiment is carried out on a micro or semi-micro scale. Very small quantities of reagents are used. Cleanliness and a great deal of care are necessary to obtain good results.

While going through the steps of analysis, you will need a copy of the appropriate flow chart available for reference. The flow charts appear at the end of the experimental directions and should be copied accurately into your lab book. The charts will help to give the "total picture" of where each analysis is and where it is heading. Read the directions carefully, and read the sections which give the notes or chemical theory for each step. Don't just follow directions "cook book" style, but make an effort to understand the chemical principles behind the procedures.

For this labwork, you do not need to write a complete lab report! Read the lab in its entirety. Start with a purpose statement and the pre-lab questions. You will have this handout available to you during the lab. You must, however, summarize the procedure taken and the results obtained. Finally answer post-lab questions after your data tables.

Keep good records. It is necessary to keep good records so as not to get confused and forget what solutions are in which tubes. Label the tubes with permanent marker so numbers do not come off in the hot water bath. Maintain a current record of the work—don't trust the results to your memory. Below is an example of the sort of record keeping that will be required in your labbook. In this example, the procedure is given on the left and results of that procedure on the right.

Step	Procedure	Known Solution		Unknown Solution	
		Results	Conclusion	Results	Conclusion
1	Add HCl to cation solution in T1. Centrifuge. Pour the supernatant into T2.	White ppt formed in T1; other ions present in T2 (blue solution)	Ag ⁺ present		

Note: T is short for tube and ppt is short precipitate. It is always good to define your abbreviations. Fill out the columns for the "Known Solution" first. Then, when analyzing the "Unknown Solution," fill out the last two columns.

Be orderly! Arrange the chemical reagents in a way so that it is easy to find the solutions needed.

Avoid contamination! Tap water is often a source of contaminating ions. It makes sense to do initial rinses of glassware with tap water, and then do a final rinse with distilled water. A stirring rod is constantly used to mix solutions, and it also must be rinsed with distilled water before use so that it does not contaminate subsequent solutions. An easy way to do this is to fill a 400-ml beaker about 2/3 full of distilled water, and keep your stirring rods in this beaker. The small amount of contaminates present in this volume of water should cause no problem. Replace the distilled water as needed.

Droppers or plastic pipets should also be rinsed twice with distilled water if they are reused. Get in the habit of rinsing items immediately after use.

Measuring Solutions: Generally, the volume of solutions added should be estimated. It is not necessary to use a graduated cylinder to measure solution volumes. For example, a tube can be calibrated in milliliters to give an idea of what volume a milliliter actually is.

Heating Solutions: Frequently it will be necessary to heat a solution to speed up a reaction. Do not heat small test tubes over Bunsen burner flames. A sudden steam bubble will cause the solution to shoot out of the test tube. Instead, heat tubes in a boiling water bath. A good idea is to set up this bath when beginning work in the lab because it may take time to heat the bath to the appropriate temperature. And remember, never, never reach over a lit burner. In this lab, plastic microcentrifuge tubes will be used. These tubes are first placed in a circular rack that then floats inside the water bath. Hot plates may be used in place of a burner set-up. Use a test tube holder when working with test tubes.

Mixing Solutions: Each time a reagent is added to a tube, the solutions need to be thoroughly mixed. Cap the microcentrifuge tube and invert in several times. You may want to also flick it vigorously with your fingers to assure adequate mixing.

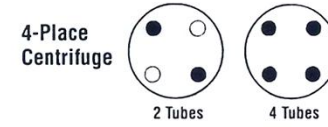
Separating Solids from Solutions: Centrifuge solutions so that the solid is packed at the bottom of the tube. Don't forget to counterbalance the tubes in the centrifuge with similar tubes holding the equivalent volumes of liquid (Figure 1). Let the centrifuge spin for about 30 seconds. Usually the supernatant liquid (the liquid above the precipitate) can be decanted (poured off) of the precipitate. Sometimes precipitates tend to float on the surface of the solution. If this is the case, use a Beral-type pipet to draw off the supernatant liquid. It is better to leave a little liquid over the precipitate than to transfer some of the precipitate.

How to Safely Load and Use a Centrifuge

- Never fill centrifuge tubes to capacity. Keep liquid levels at least 1 cm from the top.
- Label all centrifuge tubes before inserting to avoid mix-up.
- Place tubes in a symmetrical fashion, the objective being to keep the rotor balanced.
- Fill all tubes to the same height.
- If only one tube needs to be centrifuged, achieve balance by inserting an additional tube (labeled as a "blank") containing the same volume of liquid.

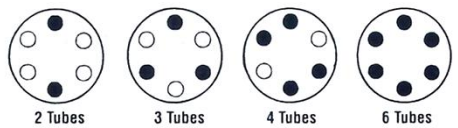
Figure 1

4-Place Centrifuge



2 Tubes 4 Tubes

6-Place Centrifuge



2 Tubes 3 Tubes 4 Tubes 6 Tubes

Washing Precipitates: It is almost always necessary to wash precipitates to free them from ions that might cause confusion in later steps. To do this, add 0.5-1 ml of distilled water to the precipitate, agitate, centrifuge, and discard wash water. Sometimes the directions will require a specific reagent in the wash water.

Checking the pH: To check the pH of a solution, put a piece of litmus paper or pH paper on a clean glass plate or watch glass. Dip the stirring rod into the solution in the tube, and touch the stirring rod to the paper (See Figure 2). Do not dip the test paper into the test tube. This may cause some of the indicator dye to dissolve into the solution, and the indicator color may confuse subsequent test.

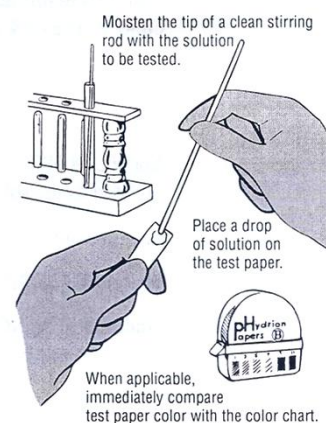


Figure 2. Using pH test

Storing Solutions: To keep a solution until the next laboratory period, make sure the solution is properly covered (e.g., tube is capped, parafilm, or stoppered). If a precipitate is present, put a few drops of distilled water on it before covering. Be sure to record a list of substances that are present in each tube. Don't rely on memory. Lastly, make sure your items are clearly labeled with your group's identification.

Pre-lab Questions Use the flow charts at the end of the experimental procedure to answer the following questions. In each question, a test is carried out to determine the presence or absence of several ions. Only those listed may be present. State if the tests indicate if each ion is present, absent, or undetermined.

1. Test for Ag^+ , Cu^{2+} , and Fe^{3+}

Some 6 M HCl is added to a solution that may contain the above ions. A white precipitate forms.

Ions present: _____ Ions absent: _____ Ions undetermined: _____

2. Test for Test for Cu^{2+} , Ag^+ , and Zn^{2+}

Some 6 M HCl is added to a solution that may contain the above ions. No precipitate forms. The addition of 6 M NaOH until the solution is basic results in no formation of precipitate.

Ions present: _____ Ions absent: _____ Ions undetermined: _____

3. Test for Cu^{2+} , Fe^{3+} , and Zn^{2+}

Some 6M NaOH is added to a clear solution that may contain the above ions until the solution is basic. A dark precipitate forms. The precipitate totally dissolves in 6 M H_2SO_4 . The addition of 6 M NH_3 to this acidic solution until it is basic results in a clear solution containing a dark precipitate. The dark precipitate completely dissolves in 6 M H_2SO_4 .

Ions present: _____ Ions absent: _____ Ions undetermined: _____

4. Test for CO_3^{2-} and Cl^-

Some 6 M HCl is added to a solution that may contain the above ions. Formation of bubbles is noted as the solution is heated.

Ions present: _____ Ions absent: _____ Ions undetermined: _____

5. Test for Cl^- , SO_4^{2-} , CO_3^{2-} , and NO_3^-

Addition of AgNO_3 causes no precipitate to form. Addition of BaCl_2 to fresh solution also causes no precipitate to form.

Ions present: _____ Ions absent: _____ Ions undetermined: _____

Only one of each of the following pairs of reactants undergoes a reaction. Write the net ionic equation for the reaction that occurs.

6. $\text{NaCl}(\text{aq}) + \text{BaCl}_2(\text{aq}) \rightarrow$ 7. $\text{NO}_3^-(\text{aq}) + \text{OH}^-(\text{aq}) + \text{Al}(\text{s}) \rightarrow$ 8. $\text{K}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow$
 $\text{Na}_2\text{SO}_4(\text{aq}) + \text{BaCl}_2(\text{aq}) \rightarrow$ $\text{CO}_3^{2-}(\text{aq}) + \text{OH}^-(\text{aq}) + \text{Al}(\text{s}) \rightarrow$ $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow$

Safety Precautions:

Silver nitrate is mildly toxic, irritating to body tissue, and stains skin and clothing. Cupric nitrate, zinc nitrate, and ferric nitrate are mildly toxic and irritating to body tissue. Barium hydroxide and barium chloride solutions are toxic by ingestion. Potassium thiocyanate solution is slightly toxic by ingestion. Avoid contact with concentrated acids since toxic hydrogen cyanide gas may be liberated. Concentrated ammonia (ammonia hydroxide) solution and hydrochloric acid solutions are toxic by inhalation, ingestion, and are corrosive to all body tissues. Sulfuric acid, nitric acid, and sodium hydroxide solutions are

severely corrosive to eyes, skin, and other tissues, and toxic by ingestion. Acidic acid solution is a corrosive liquid. Wear goggles at all times and wash hands thoroughly before leaving laboratory.

Materials

Cation solution, 5 ml

Silver nitrate, AgNO_3 , 0.05 M

Cupric nitrate, $\text{Cu}(\text{NO}_3)_2$, 0.05 M

Zinc nitrate, $\text{Zn}(\text{NO}_3)_2$, 0.05 M

Ferric nitrate, $\text{Fe}(\text{NO}_3)_3$, 0.05 M

Hydrochloric acid solution, HCl , 6 M, 10 ml

Ammonia solution, NH_3 , 6 M, 10 ml

Sulfuric acid solution, H_2SO_4 , 6 M, 10 ml

Sodium hydroxide solution, NaOH , 6M, 8 ml

Acidic acid solution, CH_3COOH , 6 M, 10 ml

Potassium thiocyanate solution, KSCN , 0.1 M, 5 ml

Potassium ferrocyanide solution, $\text{K}_4[\text{Fe}(\text{CN})_6]$, 0.1 M, 5 ml

Silver nitrate solution, AgNO_3 , 0.1 M, 10 ml

Saturated Barium hydroxide, $\text{Ba}(\text{OH})_2$, 0.2 M, 10 ml

Nitric acid solution, HNO_3 , 6 M, 10 ml

Aluminum, Al , granules

Anion solution, 5 ml

Sodium chloride, NaCl , 0.05 M

Sodium carbonate, Na_2CO_3 , 0.05 M

Sodium sulfate, Na_2SO_4 , 0.05 M

Sodium nitrate, NaNO_3 , 0.05 M

Beakers, 400-ml and 200-ml

Microcentrifuge

Microcentrifuge tubes, 1.5 ml capacity

Microcentrifuge tube racks

Litmus or pH paper

Microscope slide or watch glass

Beral-type pipets

Spatula, stirring rods, hot plate

glass test tubes (13 x 100 mm)

cotton balls

Procedure

QUALITATIVE ANALYSIS OF CATIONS

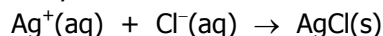
Note that the following directions are written for a known solution that contains all of the cations. An unknown solution will probably not form all of the products described in this procedure. Make note of any differences in the unknown solution as it is analyzed.

In the directions that follow, a description of the physical properties and the chemistry of the substances appears in boxed frames:

Aqueous solutions of Ag^+ and Zn^{2+} are colorless; Fe^{3+} has a yellow color and Cu^{2+} is blue.

1. Separation of the Silver from Iron, Copper, and Zinc ions.

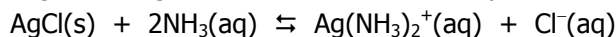
Most chloride salts are soluble; however, Ag^+ ions form insoluble chloride. These Ag^+ ions can be separated from other ions present in this qualitative analysis scheme by precipitating them as chlorides. All other ions will stay in solution.



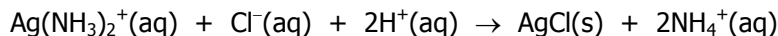
- Add 1 ml of cation solution to a tube. Add 2 drops of 6 M HCl to the solution to be analyzed. A white precipitate indicates that the Ag^+ is present.
- Centrifuge the solution and test to be sure that precipitation is complete by adding one more drop of 6 M HCl . No additional precipitate should form. If more precipitate does form, continue adding 6 M HCl until precipitation is complete.
- Centrifuge, decant (pour off), and save clear liquid into a second tube for procedure 3. Alternatively, use a Beral-type pipet to draw off supernatant liquid to transfer it to another test tube.
- Wash the precipitate by adding 1 ml of distilled water and mixing. Centrifuge and discard wash water. Save the precipitate for procedure #2.

2. Confirmation of Silver.

When 6 M NH_3 is added to AgCl , the Ag^+ ion forms a colorless complex ion and goes into solution:



Addition of HCl to the $\text{Ag}(\text{NH}_3)_2^+$ complex ion breaks apart the ion. The NH_3 combines with H^+ to form NH_4^+ , and the Ag^+ ion recombines with Cl^- ion to precipitate as white AgCl .

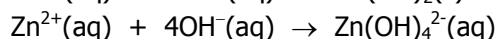
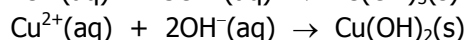
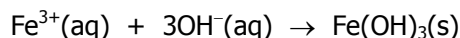


- To the precipitate from procedure 1d, which is AgCl , add 5 drops of 6 M NH_3 .
- Mix until the precipitate completely dissolves.
- Add 3 drops of 6 M HCl to the solution. The solution will smoke and the reaction between the strong acid and the base will give off heat whether or not silver is present. The tube may get very warm.
- Mix and test with pH indicator paper to be sure the solution is acidic. If it is not acidic, add more HCl . The reappearance of the white AgCl precipitate in the acidic solution confirms the presence of silver.
- Decant the supernatant into the waste container. Cap the tube and dispose of it in the garbage.

3. Separation of Iron and Copper from Zinc.

In a basic solution, the amphoteric (can display both acidic and basic properties) zinc will form a colorless complex ion and remain in solution, while the hydroxides of all the other ions will precipitate. The iron will precipitate as rust colored $\text{Fe}(\text{OH})_3$, and the copper as blue $\text{Cu}(\text{OH})_2$.

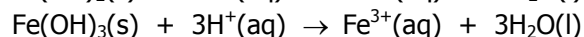
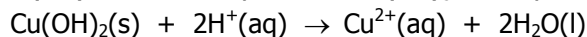
The reactions are as follows:



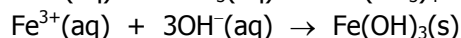
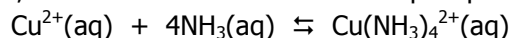
- To the solution saved from procedure 1c, add 4 drops of 6 M NaOH and mix thoroughly. Test to verify that the solution is basic with pH indicator paper. Add more NaOH , if necessary.
- Place the tube in a hot water bath for 3 minutes. The formation of a precipitate indicates the presence of either copper or iron or both.
- Centrifuge the solution, and separate the clear solution from the solid. Save the clear solution, which may contain $\text{Zn}(\text{OH})_4^{2-}$ ions for procedure #6.
- Wash the precipitate with a mixture of 5 drops of 6 M NaOH and 5 drops of water.
- Centrifuge and discard the wash water. Save the precipitate for procedure #4.

4. Separation of Iron from Copper; Confirmation of Copper.

Both cupric hydroxide, $\text{Cu}(\text{OH})_2$ and ferric hydroxide, $\text{Fe}(\text{OH})_3$, readily dissolve in acidic solution.



$\text{NH}_3(\text{aq})$ added to a solution in which Cu^{2+} ions are present, will cause the deep blue tetraammine copper (II) complex ion to form. The presence of this deep blue color confirms the presence of copper. At the same time, the basic ammonia solution will precipitate the hydroxide of iron.



An additional and very sensitive confirmatory test for copper is to precipitate the red-brown copper (II) ferrocyanide, $\text{Cu}_2[\text{Fe}(\text{CN})_6]$, from a Cu^{2+} solution.

4. Separation of Iron from Copper; Confirmation of Copper (continued).

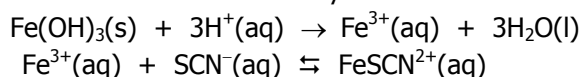
- To the precipitate from procedure 3, add 2 drops of deionized water.
- Add 2 drops of 6 M H_2SO_4 and verify with pH indicator paper that solution is acidic. Add more H_2SO_4 , if necessary. Mix to dissolve precipitate.
- To the solution, add 6 drops of 6 M aqueous NH_3 and verify that the solution is basic with pH indicator paper, and then add 4 drops more of 6 M NH_3 extra.
- Centrifuge and separate the supernatant liquid from the precipitate. Save the precipitate for procedure #5. The presence of the blue $(\text{Cu}(\text{NH}_3)_4)^{2+}$ ion is the confirmatory test for copper.

Note: For an additional confirmatory test, to the solution containing the $(\text{Cu}(\text{NH}_3)_4)^{2+}$ add 6 M CH_3COOH until the blue color fades and the solution becomes acidic. Then add 2 drops of 0.1 M $\text{K}_4[\text{Fe}(\text{CN})_6]$. A red-brown precipitate of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ reconfirms the presence of copper.

- Disposal: if you did the additional confirmatory test, give this tube to your instructor for disposal. Otherwise, decant supernatants in liquid waste containers and dispose of tubes with precipitates in garage.

5. Confirmation of Iron.

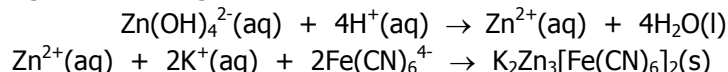
Ferric hydroxide will dissolve in sulfuric acid. Addition of the thiocyanate ion, SCN^- , forms a deep wine-red colored complex ion with iron that is a very sensitive test for the presence of iron.



- Wash the precipitate of iron hydroxides from procedure 4d.
- Add 6 M H_2SO_4 dropwise until the precipitate dissolves.
- To the solution add 1-2 drops of 0.1 M KSCN solution. The deep red FeSCN^{2+} ion confirms the presence of iron.
- Decant supernatants in liquid waste containers and dispose of tubes with precipitates in garage.

6. Confirmation of Zinc.

The confirmatory test for zinc is the formation of a precipitate of potassium zinc hexacyanoferrate, $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$. This precipitate is nearly white if pure, but if a trace of iron is present, it may appear light green or blue-green in color.



- Make the solution from procedure 3c slightly acidic by adding 6 M HCl dropwise. Verify with pH indicator paper.
- Add 1 drop of 0.1 M $\text{K}_4[\text{Fe}(\text{CN})_6]$ and mix.
- Centrifuge and see the confirmatory precipitate of $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$, which will be white to light green or blue-green in color.
- Give this tube to your instructor for disposal.

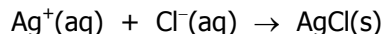
7. Repeat steps 1-6 for the unknown cation sample. Be sure to record the results for each step.

QUALITATIVE ANALYSIS OF ANIONS

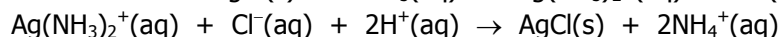
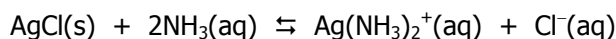
Obtain both the anion known and unknown solutions. As with the analysis of cations, record the results of each step.

1. Separation and Confirmation of Chloride.

Chloride ion forms a white, insoluble silver compound.



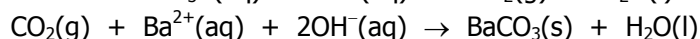
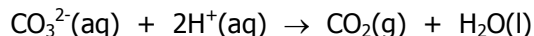
Silver chloride dissolves in ammonia, forming the colorless $\text{Ag}(\text{NH}_3)_2^+$ ion. If nitric acid is added to a solution containing this ion, the ammonia in the complex reacts with hydrogen ions to form ammonium ions, and the silver recombines with the chloride ions.



- Place 5 drops of the anion solution in a tube. Test to see if the solution is acidic. If it is not, add 6 M CH_3COOH dropwise with mixing until solution is acidic.
- Add 5 drops of 0.1 M AgNO_3 .
- If a precipitate of AgCl forms, centrifuge, and pour off the supernatant liquid as waste.
- Wash the solid with 0.5 ml of water, centrifuge and discard the wash liquid.
- Add 0.25 ml of 6 M NH_3 to the precipitate. Mix to dissolve any AgCl precipitate.
- Centrifuge and pour the supernatant liquid into another tube to test for chloride.
- Add 0.5 ml of 6 M HNO_3 to the solution. The solution will get hot and smoke from the reaction with the excess ammonia whether or not the chloride ion is present.
- Test with pH indicator paper to see if the solution is acidic. If not, add more HNO_3 . The appearance of the white precipitate AgCl in the acidic solution confirms the presence of chloride.
- Decant the supernatant into liquid waste container and discard capped tube in garbage.

2. Confirmation of Carbonate.

In acidic solution, carbonate forms carbon dioxide gas and water. The carbon dioxide may be seen as a slight effervescence. Carbon dioxide is less soluble in hot water than cold water. When carbon dioxide gas is passed through a saturated solution of barium hydroxide, it readily forms a white precipitate of barium carbonate.



If any bubbles were formed when acid was added to the original solution in #1, carbonate is probably present and carbon dioxide was formed. Confirm the presence of carbonate by reacting evolving carbon dioxide with barium hydroxide.

- Place 2 ml of clear, saturated $\text{Ba}(\text{OH})_2$ solution in a glass test tube to be available for the test with carbon dioxide.
- Place 1 ml of anion solution in a different glass test tube. Acidify the solution by adding 0.5 ml of 6 M HNO_3 . Holding the test tube with a test tube holder, place it into a hot water bath and observe to see if any gas bubbles form.
- Remove the test tube from the water bath. Take a Beral-type pipet and squeeze the bulb closed. Place the tip of the pipet close to (but not touching) the surface of the liquid in the test tube and slowly release the bulb to draw escaping carbon dioxide into the pipet.
- Put the pipet into the barium hydroxide solution, and slowly squeeze the bulb, causing the gas in the pipet to bubble through the barium hydroxide solution. This procedure may be repeated. The formation of a cloudy white precipitate of barium carbonate confirms the presence of carbonate ion in the original sample.
- Decant liquids into waste container. Place tube containing barium hydroxide in broken glass container. Rinse other tube for step #3.

3. Confirmation of Sulfate.

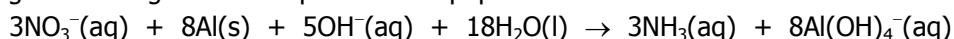
The test for sulfate is the formation of white, insoluble barium sulfate. This solid is insoluble even in acidic solution.

$$\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$$

- Place 0.5 ml of anion solution in glass test tube.
- Add 6 M HNO_3 dropwise until the solution is acidic. Verify with pH indicator paper.
- Add 0.5 ml of 0.2 M BaCl_2 solution. The formation of a white precipitate of BaSO_4 confirms the presence of sulfate.
- Decant liquid to waste container and place test tube in broken glass container.

4. Confirmation of Nitrate.

The test for nitrate involves the reduction of nitrate ions in basic solution to ammonia using solid aluminum as the reducing agent. When the solution is heated, ammonia gas is liberated. The evolving ammonia gas will turn pH indicator paper blue.



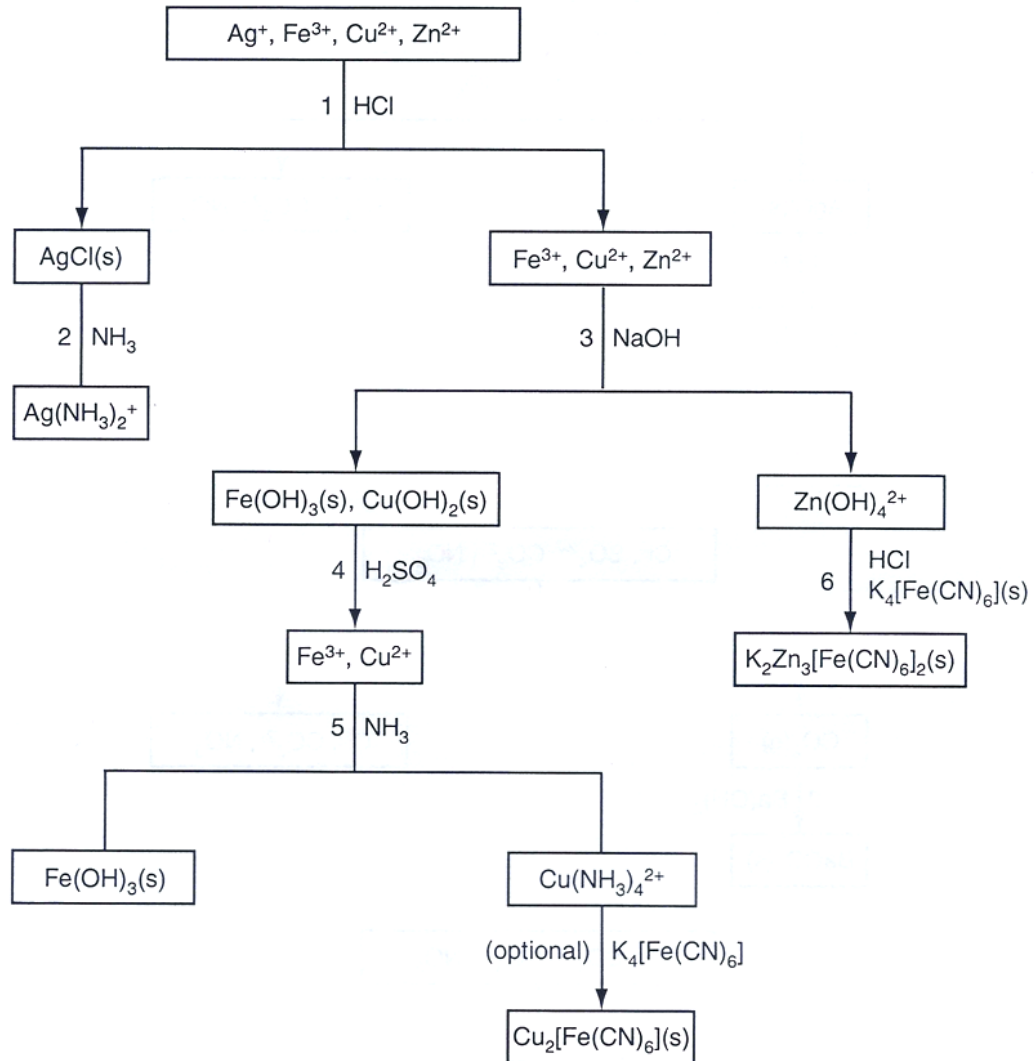
- Place 1 ml of the anion solution in a test tube.
- Add 6 M NaOH dropwise until the solution is basic, and then add 6 drops in excess.
- Use a Beral-type pipet to transfer the solution to the bottom of a dry test tube without getting the walls of the test tube wet with solution.
- Add the tip of a spatula containing aluminum granules.
- Place a small cotton wad loosely about halfway down the test tube, but not touching the solution. This is to prevent spattering of the solution onto the test paper.
- hang a piece of moist pH paper in the tube so that the bottom of the paper is close to (but not touching) the cotton.
- Using a test tube holder, warm the solution in a hot water bath until it starts bubbling strongly. Be sure that the solution and the cotton do not touch the litmus paper.
- Allow the solution to cool. A slow color change (within 3 to 5 minutes) of the indicator paper, starting at the bottom and spreading to the top, indicates the evolution of ammonia and confirms the presence of nitrate ion in the original solution.

5. Repeat steps 1-4 for the unknown anion sample.

Post-Lab Questions

- What is the precipitating reagent for silver ions? Would a solution of NaCl work as well? Explain.
- In the analysis scheme, Ag^+ is precipitated as AgCl , the precipitate is dissolved, and then the AgCl is precipitated again in the confirmatory step. Explain the chemistry of each of these steps by showing a balanced equation for each.
- when Fe^{3+} and Cu^{2+} react with NH_3 solution, they form two different types of products. One is a precipitate and one is a complex ion in solution. Write equations for these two reactions.
- Write separate oxidation and reduction half-reactions for the procedure used in the test for nitrate ions.
- In the nitrate test, why must care be taken to keep the moist litmus from coming in contact with the cotton or the solution?
- In steps 4, Ba^{2+} is added to the solution containing all six of the anions. This precipitates BaSO_4 but not BaCO_3 . However, in step 3, the precipitation of BaCO_3 is the confirmatory test for carbonate ion. Why doesn't BaCO_3 precipitate in step 4 but does in step 3?

Qualitative Analysis of Cations Flow Chart



Qualitative Analysis of Anions Flow Chart

