AT Chemistry
Scarsdale High School

Separation and Qualitative Determination of Cations

Introduction

This laboratory activity involves an analytical procedure called qualitative analysis, in which the cations in a mixture are physically separated from each other, and then their individual identities are then verified by a confirmatory chemical test.

In the first part of the lab, a solution containing four cations (the knowns) will be analyzed using techniques for qualitative analysis of cations. In the second part, a solution containing any combination of four different cations (the unknowns) will then be analyzed to determine which cations are present and which are absent.

This experiment will be carried out on a semi-micro scale. Very small quantities of reagents will be used. Cleanliness and a great deal of care are necessary to obtain good results.

To assist you in this lab, it is a good idea to keep a flow chart of the procedure for reference. The flow chart provides an overall picture of where each step in the scheme you currently are and where you are heading.

Read directions carefully along with the chemical idea behind each step. Don't just follow directions "cook book" style, but make an effort to understand the chemical principles behind the procedures.

General Techniques for Qualitative Analysis

Keep Good Records

It is necessary to keep good records so as not to get confused and forget what solutions are in which test tubes. Number the test tubes with a China marker. Maintain a current record of the work. Don't trust the results to your memory. Below is an example from step 1 in this procedure.

		Known Solution		Unknown Solution	
Step	Procedure	Results	Conclusion	Results	Conclusion
1	Add HCl to known solution in TT1. Pour ions present in solution	white ppt forms	Ag^+ present		Centrifuge. the colored solution into TT2. in TT2.

Note: TT is short for test tube and ppt is short for precipitate. Fill out the "Known Solutions" first. Then, when analyzing the "Unknown Solutions," fill out the last two columns.

Avoid Contamination

Tap water is often a source of contaminating ions. Wash and rinse all glassware with distilled water. A stirring rod is constantly used to mix solutions, and it must be rinsed with distilled water 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 contaminants 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 after they are used. Get in the habit of rinsing them 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. A test tube can be calibrated in milliliters to give an idea of what volume a milliliter actually is. Note: 20 drops roughly equals 1 mL.

Heating Solutions

Frequently it will be necessary to heat a solution to speed up a reaction. **DO NOT heat a small test tube over Bunsen Burner flames**. A sudden steam bubble will cause the solution to shoot out of the test tube. Instead, heat test 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. Make sure to check the beaker for cracks in the glass before heating.

Stirring Solutions

Each time a reagent is added to a test tube, the solution needs to be stirred. It is important to mix the solutions at the top and the bottom of the test tube. A stirring rod that is flattened at the bottom can be used as a plunger to effectively mix solutions in narrow test tubes.

Separating Solids from Solutions

Centrifuge solutions so that the solid is packed at the bottom of the test tube. Don't forget to counterbalance the test tubes in the centrifuge with similar test tubes holding equivalent volumes of liquid (Figure 1on next page). Let the centrifuge spin for about 30 seconds. Usually the supernatant liquid (the liquid above the precipitate) can be poured off 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.

- 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.
- Follow manufacturer's directions.
- 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.

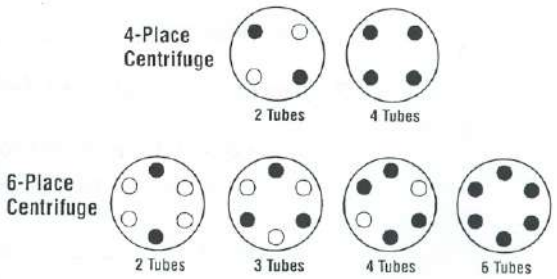

Figure 1. How to safely load and use a centrifuge.

Washing Precipitates

It is almost always necessary to wash precipitates to free them from ions that might cause contamination in later steps. To do this, add 1 or 2 mL of distilled water to the precioitate, stir, centrifuge, and discard the 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 test tube, and touch the stirring rod to the paper (see Figure 2 below). **DO NOT** dip the test paper into the test tube. This may cause some of the indicator dye to dissolve in the solution, and the indicator color may confuse subsequent tests.

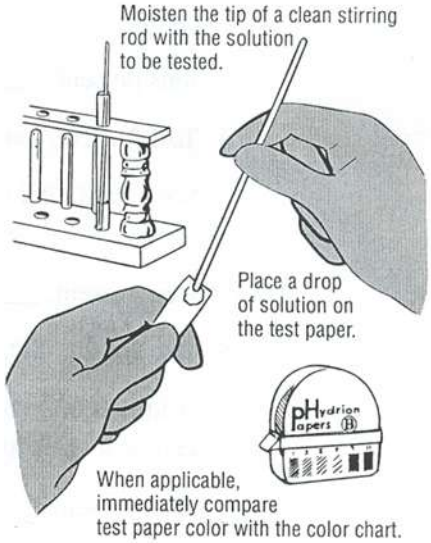

Figure 2. Using pH test paper

Storing Solutions

To keep a solution until the next laboratory period, stopper the test tube with a rubber stopper. If a precipitate is present, put a few drops of distilled water on it before stoppering the test tube. Be sure to record a list of substances that are present in each test tube. Don't rely on memory!

Safety Precautions

As stated in the introduction, we will use minimum amounts of reagents. **You must wear eye goggles at all times**. The silver nitrate solution is mildly toxic and irritating to body tissues. It also stains skin and clothing (as silver ion is reduced to silver metal in the presence of light) so the stains will appear black. **Use gloves when handling the silver nitrate**. Use caution with all other chemicals. If you spill some on your hands, wash with plenty of water. At the conclusion of each lab session, wash hands with soap and water.

Procedure

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 appear in itallic:

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

1. **Separation of Silver from Iron, Copper, and Zinc Ions.**

   Most chloride salts are soluble; however, Ag^+ ions form an 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.

   $$Ag^+ + Cl^- \rightarrow AgCl(s)$$

   a) Add 8 drops of 6 M HCl to the solution to be analyzed. Stir. A white precipitate indicates that the Ag^+ ion is present.

   b) Centrifuge the solution and test to be sure that precipitation is complete by adding one more drop of 6 M HCl. No additional precipitation should form. If more precipitate does form, continue adding 6 M HCl until precipitation is complete.

   c) Centrifuge, decant (pour off), and save the clear liquid into a second test tube for procedure 3. Alternatively, use a Beral-type pipet to draw off the supernatant liquid to transfer it to another test tube.

   d) Wash the precipitate by adding 1 mL distilled water and stirring. Centrifuge and discard the wash solution. 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:

$$AgCl(s) + 2NH_3(aq) = Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

Addition of hydrochloric acid to the $Ag(NH_3)_2^+$ complex ion breaks apart the ion. The NH_3 combines with H+ to form NH_4^+, and the Ag^+ ion recombines with the Cl^- ion to precipitate as white AgCl(s)

a) To the precipitate from procedure 1d, which is AgCl, add 1 mL 6 M NH_3.

b) Stir until the precipitate completely dissolves. You will need to use the pipette to stir the bottom of the centrifuge tube.

c) Add 15 drops of 6 M HCl to the solution. The solution will smoke and the reaction between the strong acid and base will give off heat whether or not silver is present. The test tube may get very warm.

d) Stir and test with pH indicator paper or litmus 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.

3. Separation of Iron and Copper from Zinc.

In a basic solution, the amphoteric zinc will form a colorless complex ion and remain in solution, while the hydroxides of all other ions will precipitate. The iron will precipitate as rust colored $Fe(OH)_3$, and the copper as blue $Cu(OH)_2$. The reactions are as follows:

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

$$Cu^{2+}(aq) + 2OH^-(saq) \rightarrow Cu(OH)_2(s)$$

$$Zn^{2+}(aq) + 4OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq)$$

a) To the solution saved from procedure 1c, add, with stirring, 6 M sodium hydroxide, NaOH, until the solution is basic and then add 3 more drops.

b) Stir and place the test tube in a hot water bath for 3 minutes. The formation of a precipitate indicates the presence of either copper or iron or both.

c) Centrifuge the solution, and separate the clear solution from the solid. Save the clear solution, which may contain $Zn(OH)_4^{2-}$ ions for procedure #6.

d) Wash the precipitate with a mixture of 10 drops of 6 M NaOH and 10 drops of water.

e) Centrifuge and discard the wash solution. Save the precipitate for procedure #4.

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

Both cupric hydroxide, $Cu(OH)_2$, and ferric hydroxide, $Fe(OH)_3$, readily dissolve in acid solution.

$$Cu(OH)_2(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + 3H_2O(l)$$

$$Fe(OH)_2(s) + 3H^+(aq) \rightarrow Fe^{3+}(aq) + 3H_2O(l)$$

Aqueous ammonia added to a solution in which Cu^{2+} is 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 hydroxides of iron.

$$Cu^{2+}(aq) + 4NH_3(aq) = Cu(NH_3)_4^{2+}(aq)$$

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

An additional and very sensitive confirmatory test for copper is to precipitate the red-brown copper(II) hexacyanoferrate(II) [also called copper(II) ferrocyanide], $Cu_2[Fe(CN)_6](s)$, from a Cu^{2+} solution.

a) To the precipitate from procedure 3, add 5 drops of deionized water.

b) Add 6 M H_2SO_4 dropwise until the solution is acidic when tested with litmus paper (about 6 drops). Stir to dissolve the precipitate.

c) To the solution, add 6 M aqueous NH_3 until the solution is basic to litmus, and then add 1-mL extra.

d) Centrifuge and separate the supernatant liquid from the precipitate. Save the precipitate for procedure #5. The presence of the blue $Cu(NH_3)_4^{2+}$ ion is the confirmatory test for copper.

e) Decant the supernatant copper ion solution into the waste container at the front of the room.

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.

   $$Fe(OH)_3(s) + 3H^+(aq) \rightarrow Fe^{3+}(aq) + 3H_2O(l)$$

   $$Fe^{3+}(aq) + SCN^-(aq) = FeSCN^{2+}(aq)$$

   a) Wash the precipitate of iron hydroxides from procedure 4d with 1 mL of distilled.

   b) Add 6 M H_2SO_4 dropwise until the precipitate dissolves.

   c) To the solution add 5 drops of 0.1 M KSCN solution. The deep red $FeSCN^{2+}$ ion confirms the presence of iron.

   d) Dispose of the iron solution as directed by your teacher.

6. **Confirmation of Zinc**.

   The confirmatory test for zinc is the formation of a precipitate of potassium zinc hexacyanoferrate(II), $K_2Zn_3[Fe(CN)_6]_2$. This precipitate is nearly white if pure, but if trace of iron is present, it may appear light green or blue-green in color.

   $$Zn(NH_3)_4^{2+}(aq) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + NH_4^+(aq)$$

   $$3Zn^{2+}(aq) + 2K^+(aq) + 2Fe(CN)6^{4-}(aq) \rightarrow K_2Zn_3[Fe(CN)_6]_2$$

   a) Make the solution from procedure 3c slightly acidic by adding 6 M HCl drpowise.

   b) Add 3 drops of 0.1 M $K_4[Fe(CN)_6]$ and stir.

   c) Centrifuge to see the confirmatory precipitate of $K_2Zn_3[Fe(CN)_6]_2$ which will be white to light green or blue green in color.

   d) Dispose of the zinc precipitate and solution as directed by your teacher.

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

Cation Analysis Data Table

		Known Solution		Unknown Solution	
Step	Procedure	Results	Conclusion	Results	Conclusion
1					
2					
3					
4					
5					
6					
7					

Name_____

QA Prelab Assignment

1. Prepare a flow chart for the experimental procedures used in this qualitative analysis experiment. Outline your flow chart below:

2. Use your flow chart 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.

   a) Test for Ag^{+}, Cu^{2+}, Fe^{3+}

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

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

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

   Some 6 M HCl is added to a solution that may contain the three 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: _____

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

   6 M NaOH is added to a clear solution that may contain the three 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: _____

3. Why must gloves be worn when working with the silver nitrate solution?

4. Identify the Lewis acid and Lewis base present in the following complex ions and name the complex ion:

   a) $Fe(H_2O)_6^{3+}$ LA _____ LB _____ name_____

   b) $Cu(H_2O)_4^{2+}$ LA _____ LB _____ name_____

   c) $Ag(NH_3)_2^{+}$ LA _____ LB _____ name_____

   d) $Zn(OH)_4^{2-}$ LA _____ LB _____ name_____

   e) $Cu(NH_3)_4^{2+}$ LA _____ LB _____ name_____