

Lab #13: Qualitative Analysis of Cations and Anions**Objectives:**

1. To understand the rationale and the procedure behind the separation for various cations and anions.
2. To perform qualitative analysis of two unknown solutions that contain various ions (cations and anions) and positively identify these ions using established schemes.

Materials:**Unknown Cation Solution**

(may contain some or all of the following)

- 0.05 M silver nitrate, AgNO_3 (aq)
- 0.05 M copper (II) nitrate, $\text{Cu}(\text{NO}_3)_2$ (aq)
- 0.05 M zinc nitrate, $\text{Zn}(\text{NO}_3)_2$ (aq)
- 0.05 M iron (III) nitrate, $\text{Fe}(\text{NO}_3)_3$ (aq)

- 6 M HCl (aq)
- 6 M HNO_3 (aq)
- 6 M NH_3 (aq)
- 6 M H_2SO_4 (aq)
- 6 M NaOH (aq)
- 6 M CH_3COOH (aq)
- 0.1 M KSCN (aq)
- 0.1 M potassium ferrocyanide solution, $\text{K}_4\text{Fe}(\text{CN})_6$ (aq)
- 0.1 M AgNO_3 (aq)
- Saturated $\text{Ba}(\text{OH})_2$ (aq)
- 0.1 M BaCl_2 (aq)
- Aluminum granules

Unknown Anion Solution

(may contain some or all of the following)

- 0.05 M sodium chloride, NaCl (aq)
- 0.05 M sodium carbonate, Na_2CO_3 (aq)
- 0.05 M sodium sulfate, Na_2SO_4 (aq)
- 0.05 M sodium nitrate, NaNO_3 (aq)
- 18 Test Tubes and 4 Test Tube Racks
- 400 mL Beaker (Waste)
- 250 mL Beaker
- Spatula
- 6 Beral-type Pipets
- Hot Plate
- Stirring Rods
- 6 Small Test Tube Stoppers
- Litmus or pH Paper
- Watch Glass
- Centrifuge

Background Information:

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.

To begin the lab experiment, a solution containing four cations is analyzed using the techniques for qualitative analysis of cations. A second solution containing four anions is then analyzed using the qualitative scheme for anions. 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 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 the analysis, keep a copy of the appropriate flow chart available for reference. The flow charts appear on a later page are simplified versions of what you have learned from the textbook. They will help to give the “total picture” of where each analysis is and where it is heading. Read the directions carefully, and read the paragraphs that 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.

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 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.

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 1). Let the centrifuge spin for about 30 seconds. Usually the supernatant liquid (the liquid above the precipitate) can be 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.

- 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.

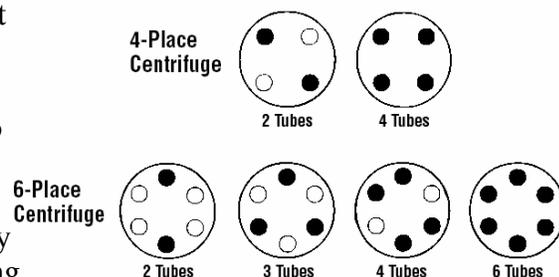


Figure 1. How to safely load and use a centrifuge.

Washing Precipitates

It is almost always necessary to wash precipitates to free them from ions that might cause confusion in later steps. To do this, add 1 or 2 mL of water to the precipitate, 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). 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 colour may confuse subsequent tests.

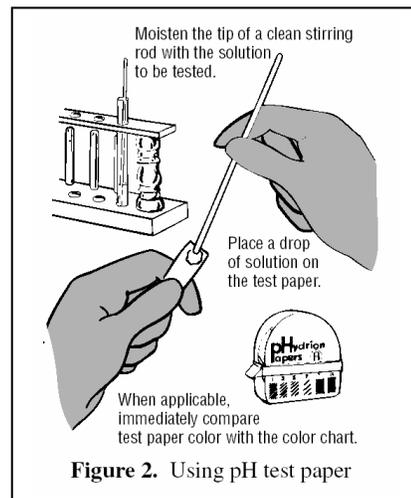


Figure 2. Using pH test paper

Safety Precautions

Silver nitrate solution is mildly toxic and irritating to body tissue. It also stains skin and clothing. Copper (II) nitrate solution is mildly toxic. Zinc nitrate solution is mildly toxic and is irritating to body tissue. Ferric nitrate solution is 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 (ammonium hydroxide) solution and hydrochloric acid solutions are toxic by inhalation, ingestion, and are corrosive to all body tissues. Sulfuric acid solution and sodium hydroxide solution are severely corrosive to eyes, skin, and other tissue. Nitric acid solution is severely corrosive, a strong oxidant, and toxic by ingestion and inhalation. Acetic acid solution is a corrosive liquid. Wear chemical splash goggles, and a chemical-resistant apron. Wash hands thoroughly with soap and water before leaving the laboratory.

Procedure:**Part A: 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.

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

- 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 precipitate 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.
- *1.5 d. Wash the precipitate by adding 1 mL distilled water and stirring. Centrifuge and discard the wash water. Save the precipitate for procedure #2.

2. Confirmation of Silver.

- a. To the precipitate from procedure 1d, which is AgCl, add 1 mL 6 M NH_3 .
- b. Stir until the precipitate completely dissolves, centrifuge, decant and test the solution in the next step (c).
- c. Add 15 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 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.
- e. Dispose of the silver compound as directed by the instructor.

3. Separation of Iron and Copper from Zinc.

- 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 $\text{Zn}(\text{OH})_4^{2-}$ 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 water. Save the precipitate for procedure #4.

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

- a. To the precipitate from procedure 3, add 5 drops of 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 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 $\text{Cu}(\text{NH}_3)_4^{2+}$ ion is the confirmatory test for copper.
- e. For an additional confirmatory test, to the solution containing the $\text{Cu}(\text{NH}_3)_4^{2+}$ add 6 M CH_3COOH , acetic acid, until the blue colour 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.
- f. Dispose of the copper solution as directed by the instructor.

5. Confirmation 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 5 drops of 0.1 M KSCN solution. The deep red FeSCN^{2+} ion confirms the presence of iron.
- Dispose of the iron solution as directed by the instructor.

6. Confirmation of Zinc.

- Make the solution from procedure 3c slightly acidic by adding 6 M HCl dropwise.
- Add 3 drops of 0.1 M $\text{K}_4[\text{Fe}(\text{CN})_6]$ and stir.
- Centrifuge to 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 colour.
- Dispose of the zinc precipitate and solution as directed by the instructor.

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

Part B: Qualitative Analysis of Anions

Obtain both the anion standards sample and the unknown anions sample. As with the analysis of cations, record the results of each step in the Anion Data Table.

1. Separation of the Chloride (Cl^-); Confirmation of Chloride.

- Place 10 drops of the original test solution (or unknown solution) in a test tube. Test to see if the solution is acidic. If it is not, add 6 M acetic acid, CH_3COOH , dropwise with stirring until the solution is acidic.
- Add 10 drops of 0.1 M silver nitrate, AgNO_3 . A precipitate of AgCl will form.
- Centrifuge and pour off the supernatant liquid.
- Wash the solid with 0.5 mL distilled water, centrifuge and discard the wash water.
- Add 0.5 mL 6 M ammonia, NH_3 , to the precipitate. Stir to dissolve any AgCl .
- Centrifuge, and pour the supernatant liquid into another test tube to test for chloride ion.
- Add 1 mL 6 M nitric acid, HNO_3 , to the solution containing the dissolved silver chloride. The solution will get hot and smoke from the reaction with the excess ammonia whether or not silver chloride is present.
- Test with litmus or pH paper to see if the solution is acidic. If it is not, add more HNO_3 until the solution is acidic. The appearance of the white precipitate of AgCl in the acidic solution confirms the presence of chloride.

2. Confirmation of Carbonate.

- Place 2 mL of clear, saturated $\text{Ba}(\text{OH})_2$ solution in a test tube to be available for the test with carbon dioxide.
- Place 1 mL of the original test solution (or unknown solution) in a different test tube.
- Acidify this solution by adding 0.5 mL of 6 M HNO_3 .
- Place the tube in a hot water bath and observe to see if any gas bubbles form.
- Take a dry 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 solution.

3. Confirmation of Sulfate.

- a. Place 0.5 mL of the original test solution (or unknown solution) in a test tube.
- b. Add 6 M nitric acid, HNO_3 , dropwise until the solution is acidic.
- c. Add 0.5 mL 0.1 M BaCl_2 solution. The formation of a white precipitate of BaSO_4 confirms the presence of sulfate.

4. Confirmation of Nitrate.

- a. Place 1 mL of the original test solution (or unknown solution) in a test tube.
 - b. Add 6 M NaOH dropwise until the solution is basic, and then add 6 drops in excess.
 - c. 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.
 - d. Add the tip of a spatula containing aluminum granules.
 - e. 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 litmus paper.
 - f. Hang a piece of moist red litmus paper (or pH paper) in the tube so that the bottom of the paper is close to (but not touching) the cotton.
 - g. 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.
 - h. Allow the solution to cool. A slow colour change (within 3 to 5 minutes) of the litmus from pink to blue, 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 anion procedures #1 – #4 for the anion unknown sample.