Experiment 7
Qualitative Analysis: Anions

I. Objective:

Determine the identity of anions in a mixture. This is accomplished by: (1) studying the chemical and physical properties of six anions and (2) then developing a chemical method for separating and identifying the six anions in an unknown solution.

II. Chemical Principles:

In this experiment and several future experiments you will be studying the chemical and physical properties of selected ions in order to determine a method for separating and identifying them in an unknown solution. The method is termed qualitative analysis.

Your instructor will review several techniques used in the experimental procedures.

- **Precipitation Techniques**:
  Precipitation of a solid occurs when the ion product for the solid exceeds the solubility product. For this experiment you will follow the directions in your lab book.

- **Heating in a Water Bath**:
  At the beginning of the period, place a beaker of water on the hot plate and bring it to a gentle boil. If a mixture requires heating, place a test tube containing the solution or heterogeneous mixture into the beaker of hot water.

- **Centrifuging a heterogeneous solution:**
  This is a technique used to separate precipitates from a solution. Ensure the solid in a mixture held in a test tube is thoroughly dispersed and not stuck to the sides of the test tube. You may have to wash down the sides of the test tube with the solvent.

  You must always have a counter test tube on the opposite side of your test tube in the centrifuge before you turn on the centrifuge. The counter test tube is a test tube with an equal volume of another solution or of water. Set the centrifuge setting to about 4 and let it spin for ~ 2 minutes. Turn off the centrifuge and let it come to a stop.
  Take out your test tube and look to see if the solid is at the bottom. If not, centrifuge it again until it does. The liquid above the solid should be clear and is called the **decantate**. It may be colored, but it should be clear.

- **Completeness of Precipitation**:
  After centrifuging a mixture with a solid add a drop or two of the precipitating agent to the liquid above your solid to insure that the solid has completely precipitated. Continue to add the reagent until you no longer observe precipitation. You may have to repeat this procedure several times.

- **Decanting a Liquid from a Solid**.
  If the precipitate is packed in the test tube and does not move you can simply pour the solution off. If the precipitate is light and fluffy and is easily disturbed, then you must decant slowly. To pour the solution from a test tube without the solid, hold a clean, glass stirring rod to the open end of the test tube. The solution will flow down the length of the rod into another test tube and any solid should remain in the test tube or on the stirring rod. In some cases you can use a capillary pipet to remove the excess liquid.

- **Washing Solids**:
  After centrifuging and separating the solid from the supernatant liquid the solid will still be wet from the precipitating reagent. To wash the solid add the indicated amount of wash liquid (quite often water) to the tube and mix well with a glass stirring rod. After mixing thoroughly, centrifuge, and decant off the wash liquid. The wash can be discarded unless otherwise indicated. You should wash precipitates at least twice. If you do not do this step unwanted ions may remain with the precipitate and will interfere with future identification test.

- **Evaporating a Liquid**:
  To reduce the volume of liquid in a test tube you must heat the liquid gently and slowly in either a test tube in a water bath or in an evaporating dish. If you warm it too quickly your compound could decompose. Heat it gently to the desired degree of reduced volume. Do not evaporate to dryness.

- **Transferring a Solid:**
  Transferring a solid from one test tube to another is accomplished by using a liquid that does not dissolve the solid. Once the liquid is added, stir the mixture to cause the solid to be suspended, and then transfer to the second test tube. Then centrifuge the mixture and remove the supernatant liquid. To transfer a solid to another type of vessel a clean, dry "rubber policeman" is used.

- **Adjusting the pH of solutions:**
  Many reactions will only occur if they are done in an acidic or basic environment. If the solution must be acidic, add a drop of acid to the solution. Moisten the end of a glass stirring rod with the solution and then touch it to pH paper. **<u>If blue litmus paper turns red, the solution is acidic. If red litmus paper remains red, the solution is acidic. In some cases a more exact pH is required and you use pH paper. Try to minimize dilution of the unknown solution.</u>**

- **Recording procedures and observations:**
  Anions have specific reactions and you will learn these by doing some chemical reactions with solutions containing known anions. You must **be very observant** and write down your experimental procedures as done and your observations in detail **in your laboratory notebook**. **Examples of details to be recorded are listed on the next page:**

1. Experimental procedures as done. Establish a format in your laboratory notebook that enables you and your instructor to easily review your experimental procedures and observations. An example of a possible format is:
    a. Develop a title or descriptor for each experimental procedure.
    b. Record experimental procedures and observations as you do them.
    c. Summarize key experimental observations
2. Reagents and their concentrations
3. pH of the solutions.
4. Formation of a precipitate, including nature and color of solid.
5. Formation of a gas. (not just the escape of air bubbles)
6. A color change in the solution.
7. A significant heating or cooling of the solution resulting from the reaction.
8. Disappearance of a precipitate.

- **Anion analysis:**

  Anion analysis is usually performed in a series of steps involving chemical reactions. You will study several chemical reactions of a group of anions to assist you in developing a procedure to separate and identify the anions in a mixture. As you carry out the experimental procedures you should note that there are several key steps in the separation and identification process:

1. Addition of $AgNO_3$ under acid conditions to determine which anions form insoluble silver salts.
2. Addition of $Ba(C_2H_3O_2)_2$ under slightly basic conditions to determine which anions form insoluble barium salts.
3. Addition of a strong acid to the anions to determine if a gas forms.
4. Addition of an oxidizing agent such as $KMnO_4$ under acid conditions to determine if an anion is oxidized.
5. Addition of ammonia to an insoluble salt of an anion to determine if a metal complex ion forms.
6. Special tests which are unique for a specific anion.

In this experiment you will develop a qualitative analysis scheme, a diagram that shows how to separate and identify the following anions: **Cl^-, I^-, SO_4^{2-}, CO_3^{2-}, NO_3^-, PO_4^{3-}**

III. Experimental Procedures:

A. General Procedures:

1. All glassware used in this experiment must be free of interfering contaminants. Thus, before you start class each period you must clean your test tubes with soap and deionized water and rinse them thoroughly with deionized water. You do not have to fill the test tube with deionized water; only the water in contact with the surface of the glass rinses the surface. Invert the test tubes in your test tube rack to allow the water to drain and to keep dust out.

2. At the start of each laboratory place a beaker of deionized water bath on a hot plate and heat the water until it gently boils (not vigorously). It will be used daily for heating solutions that are in test tubes.

3. Record all experimental observations as per requirements listed on previous page. At the end of your experimental procedures and observations you are to summarize your observations using the following table in your laboratory notebook. You should construct this table in a landscape mode rather than in a portrait mode.

Table I. Description..

	----$AgNO_3$ tests- Proc 1-- Procedure 1				$Ba(C_2H_3O_2)_2$ tests Procedure 2		Oxidizing Rxns Proc 3		Special 4 & 5	
Anion	$AgNO_3$	Add HNO_3	Add NH_3	Add HNO_3	$Ba(C_2H_3O_2)_2$	Add HNO_3	H_2SO_4	$KMnO_4$	$(NH_4)_2MoO_4$	Nitrate Test
Cl^-										
I^-										
SO_4^{2-}										
NO_3^-										
CO_3^{2-}										
PO_4^{3-}										

B. <u>Specific Procedures:</u>

1. Place 3 drops of one of the anions solutions into two test tubes and repeat for each of the other anion solutions. (making a total of twelve test tubes). Add a few drops of 0.10 M $AgNO_3$ into each of the twelve test tubes and record your observations. If a precipitate forms in any test tube, centrifuge and decant the supernatant liquid. You should have two test tubes for each anion which formed a precipitate with silver (I) nitrate. To one of the test tubes containing a solid add 6 M HNO_3 and to the other test tube slowly add about ½ mL of 15 M NH_3 (concentrated solution). Mix each mixture thoroughly using a clean, glass stirring rod. [Note: If the solid only disperses in the acid or base, it is not soluble]. If a solid dissolves in ammonia, <u>add 6 M nitric acid until the pH of the solution is acidic</u>. ***Check the pH***. Record whether a solid forms or does not.

2. Place 3 drops of one of the anions solutions into a test tube and repeat for each of the other anion solutions. Add a few drops of 0.1 M $Ba(C_2H_3O_2)_2$ to each. If a precipitate forms, centrifuge, decant, and test the solubility of the solid in 3 M HNO_3.

3. (a) Place 3 drops of one of the anions solutions into a test tube and repeat for each of the other anion solutions. To each, add 3 drops of 6 M H_2SO_4 and mix well. Note any **effervescence** (bubbling) or other changes.

(b) To each of the test tubes from part (a), add 2 drops of 0.02 M $KMnO_4$ and stir. If a reducing anion is present, MnO_4^- will form Mn^{2+}. In the hood, add 20 drops of hexane, a nonpolar organic solvent, to each of the solution and shake vigorously. Observe any color change in the **hexane layer**. Only nonpolar or weakly nonpolar substances will leave the water layer and be extracted into the hexane layer. Why? Molecular iodine is a nonpolar molecule. Why? The net ionic equations showing the reactions of iodide ion and the formation of molecular iodine are shown below:

$$SO_4^{2-} + 2\,I^- + 4\,H^+ \rightarrow SO_2 + I_2 + 2\,H_2O(l)$$

$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \rightarrow 2\,Mn^{2+} + 5\,I_2 + 8\,H_2O(l)$$

4. Place 3 drops of one of the anions solutions into a test tube and repeat for each of the other anion solutions.. Check that the solutions are acidic. Adjust the pH of any basic solutions using nitric acid (3 M). Carefully heat the solutions in a water bath for a minute. Do not let the solutions evaporate.

   Add about 3 drops of the ammonium molybdate solution to each of the solutions. If a yellow solid forms it should be $(NH_4)_3PO_4{\cdot}12MoO_3$. If there is no precipitate in the test tube containing PO_4^{3-} ion, warm the solution for a few minutes and see if it appears. The net ionic equation for the formation of the solid is:

$$3NH_4^+ + PO_4^{3-} + 12MoO_4^{2-} + 24H^+ \rightarrow (NH_4)_3PO_4.12MoO_3(s) + 12H_2O(l)$$

7. Special test for NO_3^-. Your instructor will first demonstrate this test. To a test tube containing 3 drops of a $NaNO_3$ solution and to another test tube containing a solution of NaI, add sufficient solid ferrous ammonium sulfate to saturate the solution (that means, to have a small amount of solid on the bottom of the test tube, but not a large excess). Tilt the test tube 45^o and carefully and slowly pour a small amount of fresh, concentrated H_2SO_4 (Do not use 6 M H_2SO_4) down the inside of the test tube. **Do not mix the two layers**. You should see a distinct brown ring form between the two layers. The two net ionic equations for this test are:

$$3\,Fe^{2+} \rightarrow 3\,Fe^{3+} + 3\,e^-$$
$$\underline{3\,e^- + 4\,H^+ + NO_3^- \rightarrow NO + 2\,H_2O(l)}$$
1. $$3\,Fe^{2+} + 4\,H^+ + NO_3^- \rightarrow 3\,Fe^{3+} + NO + 2\,H_2O(l)$$

NO which is formed in the previous redox reaction reacts with excess Fe^{2+} to form a metal complex ion. This complex ion is brown in color and forms at the interface between sulfuric acid and the saturated solution of ferrous ion:

2. $$Fe^{2+} + NO \rightarrow [Fe(NO)]^{2+}$$

The complex ion forms a distinctive brown ring. **I^- interferes** with this test; therefore, we do not place NO_3^- and I^- in the same unknown solution.

C. Developing a Qualitative Analysis Scheme

Before you analyze an unknown solution of anions you must prepare a diagram that shows how you plan to **separate and identify** each anion in a mixture that might contain all six anions. This diagram is called a qualitative analysis flow scheme.

Prepare a rough draft of your qualitative analysis scheme for the six anions and have your instructor review it. It must be signed by your instructor before you can begin your unknown solution.

D. Check your scheme

Using your qualitative analysis scheme separate and identify the ions in a known solution containing the anions except for the nitrate ion. The NO_3^- test is done independently on a small aliquot of the known solution. Remember that if iodide ion is present in your unknown solution then it will not have nitrate ion, and vice versa. Use 5 drops of the known solution and carry out the experimental steps described in your scheme. If your results do not match the expected ones in your qualitative analysis scheme repeat the experimental procedures to ensure that you did not make a mistake in adding chemicals. If it still does not work, see your instructor. In any step of your scheme that produces a precipitate you must check for completeness of precipitation and also wash precipitates. If you fail to do this it often results in you finding false positives in terms of ions in your solution.

E. Unknown

Obtain an unknown solution from your instructor. This solution contains **one to four ions**. Record the unknown number in your laboratory notebook. Using your qualitative analysis scheme separate and identify the ions in your unknown solution. Reminder: record in detail all experimental procedures and observations.

The score for the unknown in all experiments involving qualitative analysis is determined as follows:

$$\text{Score} = (\text{maximum points}) \times \frac{\text{Number of ions correctly reported}}{\text{Number of ions in unknown} + \text{\# incorrectly reported}}$$

Note that in the scoring formula there is a factor for incorrectly reporting ions that are not in the unknown.

IV. Laboratory Report:

1. Title page with unknown number and anions present in unknown
2. Pre-lab and corrections
3. Copy of all laboratory data in laboratory notebook including Table 1. To earn high marks on qualitative analysis laboratory reports you must record complete and detailed experimental procedures and observation.
4. Rough draft of qualitative analysis scheme signed by instructor.
5. Final copy of qualitative analysis scheme, hand written on white paper, which has no errors or corrections. Each step in the qualitative analysis scheme that has a chemical reaction is sequentially numbered.
6. For each numbered step in the qualitative analysis scheme, type all net ionic equations associated with each step. Show only the final net ionic equation.
7. A typed summary statement providing your logic, with reference to experimental observations, for choosing the ions in your unknown.

V. Pre-Lab:

1. (a) Which anions in this experiment are basic anions? Why are they considered basic anions? (b) Write the net ionic equation describing the reaction of each with nitric acid.

2. Which steps in the experimental procedures require you to be careful with strong acids and bases? What do you do if you spill a strong acid or base on your skin?

3. (a) When ammonia is added to solid silver chloride what is the metal complex ion that forms? (b) If the solution containing the metal complex ion is made acidic, why will the silver chloride precipitate? Write net ionic equations describing these two reactions. This series of reactions is used in this experiment to identify and confirm the chloride ion.

4. A mixture of sodium salts may contain one or more of the anions studied in this experiment. All of the salts are readily and completely soluble in cold water. Two samples of this aqueous solution show no precipitate when $AgNO_3$ or $BaCl_2$ is added. What anions are shown to be conclusively present in the unknown solution? Which anions are shown to be definitely absent? For which anions are the tests insufficient to confirm their presence or absence. Explain your logic for each situation.

5. A mixture of sodium salts may contain one or more of the anions studied in this experiment. All of the salts are readily and completely soluble in cold water. When silver nitrate is added to the solution, a precipitate forms. What anions are shown to be conclusively present in the unknown solution? Which anions are shown to be definitely absent? For which anions are the tests insufficient to confirm their presence or absence. Explain your logic for each situation.