

## EXPERIMENT C4: QUALITATIVE ANALYSIS OF ANIONS

### Learning Outcomes

Upon completion of this lab, the student will be able to:

- 1) Analyze a given sample of an ionic compound and identify which of the following anions is present: chloride, bromide, iodide, carbonate, sulfate, phosphate, oxalate, or nitrate

### Introduction

The chemical identity of a given sample must often be analyzed in various circumstances. In the case of ionic compounds, the identification involves tests to determine the exact cation and anion in the compound. These analyses are routinely conducted in medical (blood/urine tests), environmental (water/sewer/waste), pharmaceutical (drugs), and chemical research laboratories. While the exact analytical technique may be different from that described here, the basic principles of these analyses are often the same.

In this experiment, the identification of some common anions will be explored. The underlying principle of this analysis has to do with the solubility properties of ionic compounds.

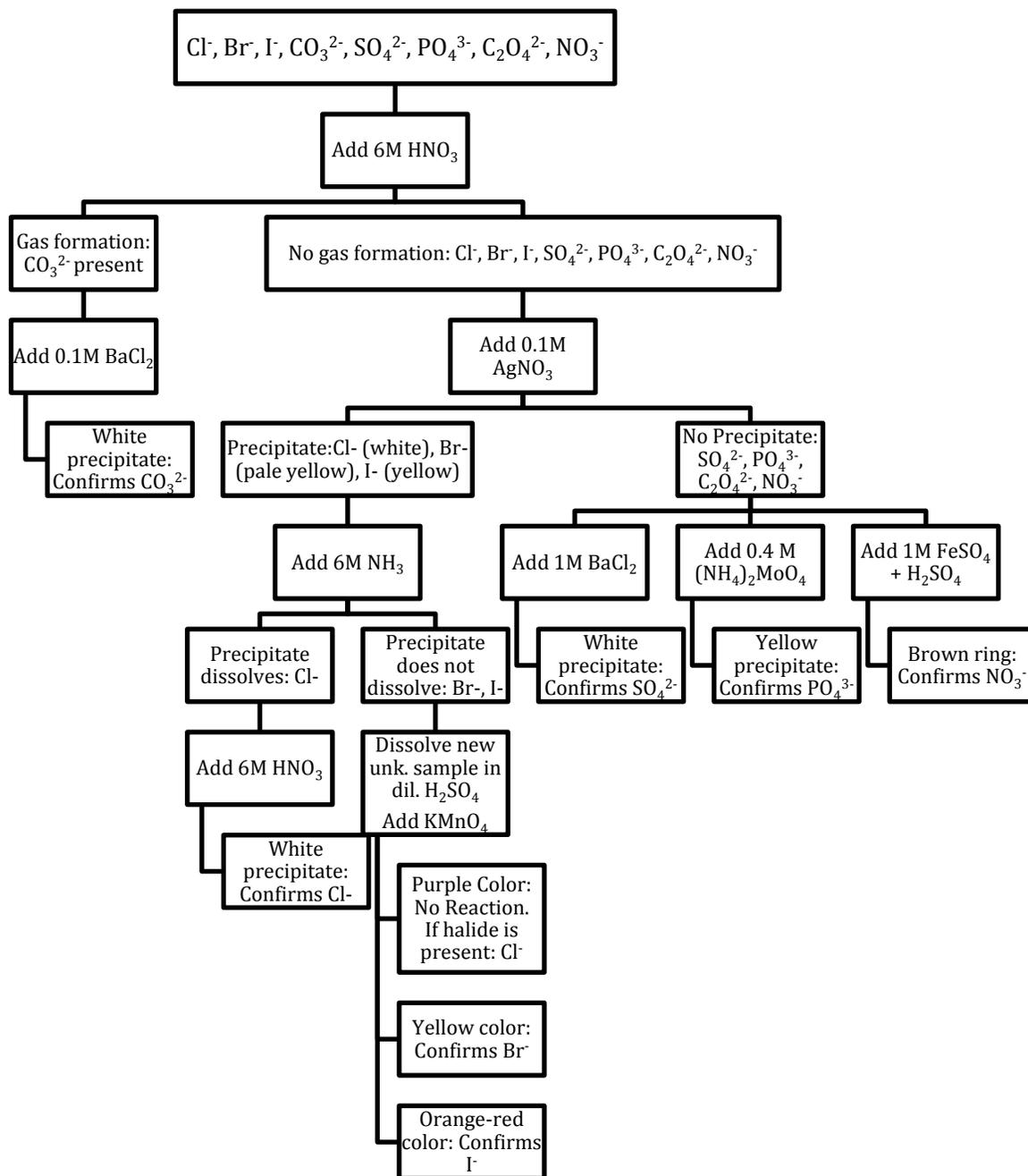
As has been previously discussed several ionic substances are only sparingly soluble in water. The solubility of a particular ionic compound depends on the solubility product constant. The solubility rules are a good guideline indicating the solubility of anions. An abbreviated set of these rules is given in Table 1 below.

Rule	Compounds containing		Exceptions
1	Group 1A cations	Soluble	None
2	NH <sub>4</sub> <sup>+</sup>	Soluble	None
3	NO <sub>3</sub> <sup>-</sup>	Soluble	None
4	CH <sub>3</sub> COO <sup>-</sup>	Soluble	None
5	Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> ,	Soluble	If the cation is: Ag <sup>+</sup> , Pb <sup>2+</sup> , Cu <sup>+</sup> , Hg <sub>2</sub> <sup>2+</sup>
6	SO <sub>4</sub> <sup>2-</sup>	Soluble	If the cation is: Ca <sup>2+</sup> , Ba <sup>2+</sup> , Sr <sup>2+</sup> , Ag <sup>+</sup> , Pb <sup>2+</sup>
7	OH <sup>-</sup>	Insoluble	Rule 1, 2 & if the cation is Ca <sup>2+</sup> , Ba <sup>2+</sup> , Sr <sup>2+</sup>
8	CO <sub>3</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup>	Insoluble	Rule 1, 2

TABLE 1

The differences in the solubility of ions and the characteristic colors of their precipitates will be used to identify the anions. The anions explored in this experiment are: chloride (Cl<sup>-</sup>), bromide (Br<sup>-</sup>), iodide (I<sup>-</sup>), carbonate (CO<sub>3</sub><sup>2-</sup>), phosphate (PO<sub>4</sub><sup>3-</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), oxalate (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>), and nitrate (NO<sub>3</sub><sup>-</sup>). The tests for

the identity of an anion is usually twofold: 1) an initial reaction to predict the possibility of a particular ion and 2) a confirmatory test specific to the particular anion in question. The following flow-chart is a depiction of the tests that will establish the identity of an anion.



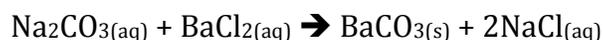
**Test for carbonate (CO<sub>3</sub><sup>2-</sup>)**

Carbonates react with concentrated acids and produce carbon dioxide gas, which is observed as effervescence in the medium.

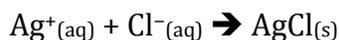


None of the other anions produce a similar reaction.

When barium ions are added to a solution containing carbonate ions, barium carbonate precipitate is formed, which serves as an additional confirmation for the presence of carbonate ions in the medium.

**Test for chloride (Cl<sup>-</sup>)**

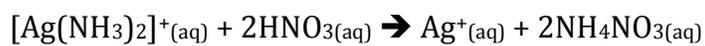
According to Table 1, silver salts of chloride ions are insoluble.



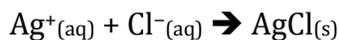
AgCl is a white precipitate that dissolves in a solution of aqueous ammonia due to the complex formation between Ag<sup>+</sup> and NH<sub>3</sub>.



Upon addition of HNO<sub>3</sub>, the following reaction occurs:

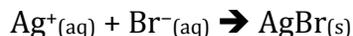


The regenerated silver ions combine with the chloride ions and reform the silver chloride precipitate.

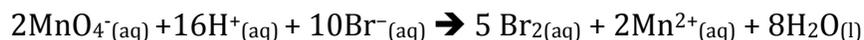


### **Test for bromide (Br<sup>-</sup>)**

According to Table 1, silver salts of bromide ions are insoluble. The pale yellow precipitate may dissolve sparingly in aqueous ammonia solutions.

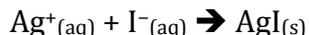


Bromide is a strong reducing agent. It will be oxidized to bromine in a red-ox reaction with  $\text{MnO}_4^-$ . The reddish brown color of the bromine may be observed in the aqueous layer

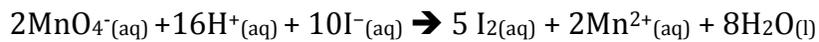


### **Test for iodide (I<sup>-</sup>)**

According to Table 1, silver salts of bromide ions are insoluble.

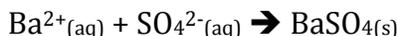


Iodide is a strong reducing agent. It will be oxidized to iodine in a red-ox reaction with  $\text{MnO}_4^-$ . The purple color of the iodine may be observed in the aqueous layer.



### **Test for sulfate (SO<sub>4</sub><sup>2-</sup>)**

The sulfate ion is the conjugate base of a strong acid (sulfuric acid). As a result, a precipitate of sulfate is insoluble in strong acids. According to Table 1, sulfate salts are generally soluble except when the cation is  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ . When aqueous barium chloride is added to an acidified solution containing sulfate ions, an insoluble precipitate of  $\text{BaSO}_4$  results. This precipitate is white in color and confirms the presence of sulfate.



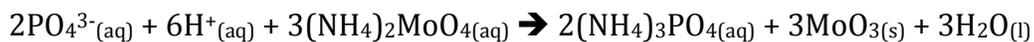
The remaining anions at this point are phosphate, oxalate, and nitrate (refer to flow-chart above). Both phosphate and oxalate are conjugate bases of weak acids (phosphoric acid and oxalic acid, respectively) and therefore their precipitates will dissolve in a strong acid.



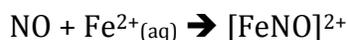
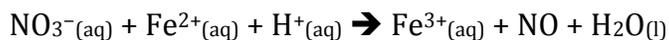
Since nitrates are always soluble (refer to Table 1), the precipitate formed from the addition of aqueous barium chloride cannot be nitrate.

**Test for phosphate (PO<sub>4</sub><sup>3-</sup>)**

Addition of aqueous ammonium molybdate to an aqueous solution containing phosphate ions results in a yellow precipitate. Other anions may also result in a precipitate with this reagent, but those precipitates are white in color.

**Test for nitrate (NO<sub>3</sub><sup>-</sup>)**

Nitrate is reduced to nitric oxide in the presence of Fe<sup>2+</sup> in an acidic medium.



The nitric oxide forms a complex with the excess Fe<sup>2+</sup>. This appears as a brown ring at the interface of the concentrated acid layer and the aqueous medium containing Fe<sup>2+</sup>.

## Experimental Design

Both known and unknown samples of soluble salts of the various anions to be analyzed are provided. Perform all the tests on the known salts first. This should be followed by the analysis of the unknown salt.

## Reagents and Supplies

Solid known and unknown samples of soluble salts of: chloride, bromide, iodide, carbonate, sulfate, phosphate, oxalate, and nitrate

Acids: 6 M HNO<sub>3</sub>, 3 M H<sub>2</sub>SO<sub>4</sub>, concentrated H<sub>2</sub>SO<sub>4</sub>, 6 M HCl

Bases: 6 M NH<sub>3</sub>

Other Reagents: 0.1 M BaCl<sub>2</sub>, 0.1 M AgNO<sub>3</sub>, dilute aqueous KMnO<sub>4</sub>, 0.4 M (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>, 1 M FeSO<sub>4</sub>

(See posted Material Safety Data Sheets)

## Procedure

### PART 1: ANALYSIS OF KNOWN SAMPLES

#### CARBONATE

1. Add 6 M nitric acid to a pinch of the solid carbonate salt. Record the observation.
2. Dissolve a pinch of the solid carbonate in a small amount of (~10 mL) deionized water.
3. In a small test tube, combine 10 drops of the above solution (from Step 2) with five drops of 0.1 M BaCl<sub>2</sub>. Record the observations.

#### HALIDES

4. In three separate labeled test tubes, dissolve a pinch of the respective halide salt in a small amount of (~10 mL) deionized water.
5. In small test tubes, combine 10 drops of the test solution (each of the three solutions from step 4 above) with five drops of 6 M HNO<sub>3</sub>.
6. Check the pH of the acidified test solution from Step 5 to ensure that the solution is acidic and add more HNO<sub>3</sub> if needed. Add five drops of 0.1 M AgNO<sub>3</sub> to the acidified test solutions. Record the observations.
7. Chloride test: Centrifuge the mixture containing the white precipitate from Step 6. Discard the supernatant. Add 10 drops of deionized water and two drops of 6 M NH<sub>3</sub> to dissolve the precipitate. The precipitate only dissolves if it is a silver chloride precipitate. To the dissolved solution, add 6 M HNO<sub>3</sub> until the solution is acidic. The reappearance of a precipitate confirms the presence of chloride ions.
8. Bromide/Iodide test: If the precipitate in Step 6 is pale yellow or darker yellow, it likely contains a bromide or iodide. Dissolve a pinch of the bromide **or** iodide salt in 10-20 drops of 0.1 M H<sub>2</sub>SO<sub>4</sub>, followed by 1-2 drops of 0.1M KMnO<sub>4</sub>.
  - a. Bromide salt test: appearance of a yellow color in the solution confirms the presence of bromide ions.
  - b. Iodide salt test: appearance of an orange-red color in the solution confirms the presence of iodide ions.

SULFATE

9. Dissolve a pinch of the sulfate salt in a small amount of (~10 mL) deionized water.
10. To five drops of the above solution from Step 9, add two drops of 6 M HCl followed by two drops of 0.1 M BaCl<sub>2</sub>. Record the observations.

PHOSPHATE

11. Dissolve a pinch of the phosphate salt in a small amount of (~10 mL) deionized water.
12. Take 10 drops of the above solution (from Step 11) and add five drops of 6 M HNO<sub>3</sub> and five drops of 0.4 M (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>. Record the observations.

NITRATE

13. Dissolve a pinch of the nitrate salt in a small amount of (~10 mL) deionized water.
14. Add five drops of 1 M FeSO<sub>4</sub> solution to 10 drops of the above solution (from Step 13) and mix thoroughly. Add 2-3 drops of 3 M H<sub>2</sub>SO<sub>4</sub> to this solution until it is acidic. Incline the test tube at a 45° angle and gently add 1 mL of concentrated H<sub>2</sub>SO<sub>4</sub> using a dropper along the sides of the test tube. Make sure that the contents of the test tube do not mix. Allow the test tube to stand for a few minutes and look for the appearance of a brown ring at the interface of the sulfuric acid layer (the bottom) and the test solution layer. Record the observations.

PART 2: ANALYSIS OF UNKNOWN SAMPLE

1. Add 6 M nitric acid to a pinch of the solid unknown. If there is effervescence, then proceed to carbonate test (Step 3).
2. Dissolve approximately 0.2 grams of the unknown solid in 25 mL of deionized water. This will be the "Test Solution". It is not necessary to measure 0.2 grams using a balance. This quantity is approximately the measure at the tip of a spatula.
3. Carbonate test: In a small test tube, combine 10 drops of the test solution (from Step 2) with five drops of 0.1 M BaCl<sub>2</sub>. The formation of a white precipitate confirms the presence of carbonate ions in the test solution. NOTE: sulfate, phosphate, and oxalate will also form white precipitates, but these ions do not produce any effervescence with nitric acid.
4. In a small test tube, combine 10 drops of the test solution with five drops of 6 M HNO<sub>3</sub>.
5. Check the pH of the acidified test solution from Step 4 to ensure that the solution is acidic and add more HNO<sub>3</sub> if needed. Add five drops of 0.1 M AgNO<sub>3</sub> to the acidified test solution. If a precipitate is observed (white: possibly Cl<sup>-</sup>, pale yellow: possibly Br<sup>-</sup>, yellow: possibly I<sup>-</sup>), then proceed for the halide tests described in Steps 6 and 7. If no precipitate is observed then proceed to Step 8.
6. Chloride test: Centrifuge the mixture containing the white precipitate from Step 4. Discard the supernatant. Add 10 drops of deionized water and two drops of 6 M NH<sub>3</sub> to dissolve the precipitate. The precipitate only dissolves if it is a silver chloride precipitate. To the dissolved solution, add 6 M HNO<sub>3</sub> until the solution is acidic. The reappearance of a precipitate confirms the presence of chloride ions.
15. Bromide/Iodide test: If the precipitate in Step 4 is pale yellow or darker yellow, it likely contains a bromide or iodide. Dissolve a pinch of the unknown salt in 10-20 drops of 0.1 M H<sub>2</sub>SO<sub>4</sub>, followed by 1-2 drops of 0.1M KMnO<sub>4</sub>.
  - a. Bromide: appearance of a yellow color in the solution confirms the presence of bromide ions.
  - b. Iodide: appearance of an orange-red color in the solution confirms the presence of iodide ions.
7. Sulfate test: To five drops of the test solution from Step 1, add two drops of 6 M HCl followed by two drops of 0.1 M BaCl<sub>2</sub>. Formation of a white precipitate confirms the presence of sulfate. Phosphate ions may also precipitate in this situation; so the phosphate test (Step 9) must be performed to confirm the presence or absence of phosphate.

8. Phosphate test: Take 10 drops of the original test solution (from Step 1) and add five drops of 6 M  $\text{HNO}_3$  and five drops of 0.4 M  $(\text{NH}_4)_2\text{MoO}_4$ . Formation of a yellow precipitate confirms the presence of phosphate. All the other anions form a white precipitate.
9. Nitrate test: Add five drops of 1 M  $\text{FeSO}_4$  solution to 10 drops of the original test solution (from Step 1) and mix thoroughly. Add 2-3 drops of 3 M  $\text{H}_2\text{SO}_4$  to this solution until it is acidic. Incline the test tube at a  $45^\circ$  angle and gently add 1 mL of concentrated  $\text{H}_2\text{SO}_4$  using a dropper along the sides of the test tube. Make sure that the contents of the test tube do not mix. Allow the test tube to stand for a few minutes and look for the appearance of a brown ring at the interface of the sulfuric acid layer (the bottom) and the test solution layer. Formation of the brown ring confirms the presence of nitrate ions in the original solution.
10. Oxalate test: The presence of oxalate in the unknown is determined by exclusion. If the unknown tests negative to all the above confirmatory tests, then based on the process of elimination, the unknown must be oxalate.

## Data Table

### PART 1: ANALYSIS OF KNOWN SAMPLES

Step	Experiment	Observation
1	Add 6 M nitric acid to a pinch of the solid carbonate salt	
3	Carbonate + 0.1 M BaCl <sub>2</sub>	
6	Chloride + HNO <sub>3</sub> + 0.1 M AgNO <sub>3</sub>	
6	Bromide + HNO <sub>3</sub> + 0.1 M AgNO <sub>3</sub>	
6	Iodide + HNO <sub>3</sub> + 0.1 M AgNO <sub>3</sub>	
7	Chloride test	
8a	Bromide test	
8b	Iodide test	
10	Sulfate + 6 M HCl followed by two drops of 0.1 M BaCl <sub>2</sub>	
12	Phosphate + five drops of 6 M HNO <sub>3</sub> and five drops of 0.4 M (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub>	
14	Nitrate + 1 M FeSO <sub>4</sub> + 3 M H <sub>2</sub> SO <sub>4</sub> + concentrated H <sub>2</sub> SO <sub>4</sub>	

PART 2: ANALYSIS OF UNKNOWN SAMPLE

		<b>Observations</b>		
<b>Step</b>	<b>Experiment</b>	<b>UNKNOWN 1</b>	<b>UNKNOWN 2</b>	<b>UNKNOWN 3</b>
1	Unknown + 6 M nitric acid			
3	Carbonate test			
5	Halide test			
6	Chloride test			
7a	Bromide test			
7b	Iodide test			
8	Sulfate test			
9	Phosphate test			
10	Nitrate test			

## Results

List the relevant observations and the identity of the unknown below:

	Unknown Number	Relevant Observations	Identify	
			Name	Formula
1				
2				
3				