Qualitative Analysis of a Group of Cations

Objective: Observe chemical reactions involving Ba^{2+}, Pb^{2+}, and Fe^{3+} ions; develop procedures to confirm the presence of these ions in an unknown solution

Materials: 0.10 M barium nitrate, $Ba(NO_3)_2$; 0.10 M iron(III) nitrate, $Fe(NO_3)_3$; 0.10 M lead(II) nitrate, $Pb(NO_3)_2$; 0.10 M potassium thiocyanate, KSCN; 0.10 M sodium sulfate, Na_2SO_4; saturated sodium acetate, $NaC_2H_3O_2$; 1 M hydrochloric acid, HCl

Equipment: Six 15 x 125-mm test tubes; 10-mL graduated cylinder; eye dropper; 250-mL beaker (for waste)

Safety: Solutions containing nitrate ions are oxidizing and should be handled carefully. Barium, lead, and thiocyanate solutions are toxic and/or irritants. Sodium sulfate solutions are irritants. Hydrochloric acid is toxic and corrosive. Wear safety goggles at all times when working at the lab bench. Students should wear gloves when handling test solutions and reagents.

Waste Disposal: All test solutions and excess reagents should be placed in the inorganic waste container as directed by the lab instructor.

Review: Molecular equations, total ionic equations, and net ionic equations.

INTRODUCTION

When chemists begin analyzing an unknown substance they ask two fundamental questions: What substances (elements/compounds) are present in the sample, and how much of each is present? To answer the first question (What is it?), chemists use **qualitative analysis** techniques. The answer to the second question (How much?) requires **quantitative analysis**.

Qualitative analysis takes advantage of differences in the chemical reactivity of elements, ions or compounds. For most inorganic qualitative analysis schemes this involves **ionic equilibria**, or reversible ionic reactions in aqueous solution. For example, mixing an aqueous solution of silver nitrate with hydrochloric acid results in the formation of silver chloride, an insoluble product called a **precipitate**, as shown in Equation (1).

$$AgNO_3(aq) + HCl(aq) \leftrightarrow AgCl(s) \text{ (white solid)} \qquad (1)$$

The reaction in Eq. (1) is called a **molecular equation** because it uses the molecular formulas of the original compounds. Both $AgNO_3$ and HCl are ionic compounds which ionize nearly 100%

in aqueous solution, so Eq. (1) could also be rewritten to show the ions that actually exist in solution. This is shown in Equation (2).

$$Ag^{+}(aq) \;+\; NO_3^{-}(aq) \;+\; H^{+}(aq) \;+\; Cl^{-}(aq) \;\leftrightarrow\; AgCl\,(s) \;+\; H^{+}(aq) \;+\; NO_3^{-}(aq) \qquad (2)$$

Eq. (2) is called the **total ionic equation** because it includes all the ions involved in the reaction. If you examine Eq. (2), however, you will note that the $H^{+}(aq)$ and $NO_3^{-}(aq)$ ions are unchanged during the reaction and appear in the same form on both the left and right sides of the reaction. They are called **spectator ions** because they are not directly involved in the reaction but are only present to maintain the balance of ionic charges. If we remove the spectator ions from both the left and right sides of Eq. (2) we obtain:

$$Ag^{+}(aq) \;+\; \cancel{NO_3^{-}(aq)} \;+\; \cancel{H^{+}(aq)} \;+\; Cl^{-}(aq) \;\leftrightarrow\; AgCl\,(s) \;+\; \cancel{H^{+}(aq)} \;+\; \cancel{NO_3^{-}(aq)} \qquad (2)$$

$$Ag^{+}(aq) \;+\; Cl^{-}(aq) \;\leftrightarrow\; AgCl(s) \qquad (3)$$

Equation (3) is called the **net ionic equation** and only includes those ions and compounds that are directly involved in the reaction.

We can use ionic equilibria to separate and identify ions in a mixture by following a carefully designed series of steps. Usually, we take advantage of the tendency of the ions to form insoluble products, or to form soluble complexes. As an example, consider the qualitative analysis data presented in Table 1for a mixture containing Ag^{+}, Ca^{2+}, and Cu^{2+}.

Table 1. Qualitative Analysis Data for Mixture of Ag^{+}, Ca^{2+}, and Cu^{2+}.

Ion	Initial soln.	1. Add 1 M Na_2CO_3	2. Add 3 M NH_3 to Soln. 1	3. Add 6 M HCl
Ag^{+}	Clear	white precipitate	ppt. dissolves	white ppt.
Ca^{2+}	Clear	white precipitate	N. R.	ppt. dissolves
Cu^{2+}	Light blue	N. R. (no reaction)	Soln. turns deep blue	---

The initial color of the sample solution can provide useful information in this case, since the Cu^{2+} ion in aqueous solution is light blue. If addition of sodium carbonate in Step 1 produces a white precipitate, then the solution may also contain either Ag^{+} or Ca^{2+} (or both). The net ionic equations for the precipitation reactions involving Ag^{+} and Ca^{2+} are given in Equations (4) and (5).

$$2\,Ag^{+}(aq) \;+\; CO_3^{2-}(aq) \;\leftrightarrow\; Ag_2CO_3(s) \qquad (4)$$

$$Ca^{2+}(aq) \;+\; CO_3^{2-}(aq) \;\leftrightarrow\; CaCO_3(s) \qquad (5)$$

The solid can be collected by decanting the **supernate**, or solution in contact with the precipitate. The presence of Cu^{2+} ion can be confirmed by adding 3 M NH_3 to the supernate; the solution will turn a deep blue. The precipitate can then be tested with 3 M NH_3 to confirm the presence of Ag^+ and/or Ca^{2+}. If all of the precipitate dissolves when NH_3 is added, then only Ag^+ is present. This is due to the formation of a soluble complex, as shown in Equation (6).

$$AgCl(s) + 2NH_3 \leftrightarrow Ag(NH_3)^+(aq) + Cl^-(aq) \quad (6)$$

If the precipitate contains $CaCO_3(s)$ it will not dissolve since Ca^{2+} does not form a soluble complex with NH_3. But what if both Ag^+ and Ca^{2+} are present? Addition of NH_3 may dissolve some, but not all, of the precipitate and the result will be ambiguous. To verify the presence of Ag^+ and Ca^{2+} an additional test is needed.

If both Ag_2CO_3 and $CaCO_3$ are present in the original precipitate, addition of NH_3 would redissolve the Ag^+ ion and it would be present in the supernate. Decanting the supernate would remove the Ag^+ ion (if present), and the Ca^{2+} would remain in the precipitate. The presence of Ag^+ in the supernate can be confirmed by adding 6 M HCl and heating the solution. If present, the Ag^+ will precipitate as AgCl(s) and the NH_3 will evaporate from solution, as shown in Equation (7).

$$Ag(NH_3)^+(aq) + Cl^-(aq) \xleftrightarrow{heat} AgCl(s) + 2NH_3(g) \quad (7)$$

Adding 6 M HCl to the precipitate and heating will cause the $CaCO_3(s)$ to dissolve as shown in Equation (8).

$$CaCO_3(s) + 2HCl(aq) \xleftrightarrow{heat} CaCl_2(aq) + H_2CO_3(aq) \quad (8)$$

In this lab exercise you will take advantage of solubility and complexation equilibria to confirm the presence of three cations: Fe^{3+}, Ba^{2+}, and Pb^{2+}. First, you will test known solutions of each of these ions individually and record your observations. Second, you will test a mixture containing all three ions and use your previous observations to confirm if the characteristic reactions for individual ions also occur when the cations are in a mixture. Finally, you will test an unknown solution and use your previous observations to identify which cations are present in the unknown.

Pre-Lab Questions

1. Briefly describe the hazards associated with each of the following chemicals, and the appropriate precautions to be taken.

   a) $Ba(NO_3)_2$

   b) 1 M HCl

   c) $Pb(NO_3)_2$

   d) KSCN

2. Discuss the difference between qualitative and quantitative analysis. Which type is utilized in this exercise?

3. In a common qualitative analysis scheme, the presence of silver ion (Ag^+) can be confirmed b adding bromide ion (Br^-) to the test solution to form silver bromide (solid). Write the balanced molecular, total ionic, and net ionic equations for the reaction between aqueous solutions of silver nitrate ($AgNO_3$) and sodium bromide (NaBr) to form solid silver bromide (AgBr).

   a) Molecular equation:

   b) Total ionic equation:

   c) Net ionic equation:

PROCEDURE

1. Label three of your test tubes with the identity of the metal cations; i.e., label the first as "Fe^{3+}, "the second as "Ba^{2+}", and the third as "Pb^{2+}". Place these test tubes in your test tube rack.

2. Label three more of your test tubes with the labels "1," "2," and "3," respectively, and place them in your test tube rack.

Note: When adding reagents in Procedures A-E, be sure to replace the droppers in the correct containers to avoid contamination. Contamination of reagent solutions may produce incorrect results and lead to invalid conclusions.

A. Reactions of Fe^{3+} Ion

3. Obtain 8 mL of 0.10 M $Fe(NO_3)_3$ solution in a clean, dry graduated cylinder. Pour about 2 mL into each of the numbered test tubes, and pour the remaining 2 mL into the test tube labeled Fe^{3+}.

4. Add 3 drops of 0.10 M KSCN solution to the $Fe(NO_3)_3$ solution in test tube 1. You can mix the solutions in the test tube by holding the test tube firmly at the top, and gently striking the bottom third of the test tube with your index finger. **Never mix the contents of a test tube by covering the opening with your finger and shaking the test tube!** Mix the solutions in the test tube thoroughly. Record your observations in the table on the Data Sheet. Indicate if a reaction occurred (Y or N) in the appropriate column in the table. If a reaction did occur, write the chemical reaction in the last column.

5. Add 15 drops of the 1.0 M HCl to the $Fe(NO_3)_3$ solution in test tube 2. Mix thoroughly, and record your observations in the table on the Data Sheet. Complete the last two columns of the table to indicate if a reaction occurred, etc.

6. Add 3 drops of 0.10 M Na_2SO_4 solution to the $Fe(NO_3)_3$ solution in test tube 3 and mix thoroughly. Record your observations and complete the last two columns in the table on the Data Sheet.

7. Discard the contents of test tubes 1, 2, and 3 into your waste beaker. Rinse each of the test tubes and the graduated cylinder twice with 5 mL portions of tap water, and twice with 5 mL portions of distilled water. Add these rinse solutions to the waste beaker.

B. Reactions of Ba^{2+} Ion.

8. Obtain 8 mL of 0.10 M $Ba(NO_3)_2$ solution in a clean, dry graduated cylinder. Pour about 2 mL into each of the numbered test tubes, and pour the remaining 2 mL into the test tube labeled Ba^{2+}.

9. Add 3 drops of 0.10 M KSCN solution to the $Ba(NO_3)_2$ solution in test tube 1. Mix the solutions in the test tube thoroughly. Record your observations in the table on the Data Sheet, and indicate if a reaction occurred (Y or N). If a reaction did occur, write the chemical reaction in the last column.

10. Add 15 drops of the 1.0 M HCl to the $Ba(NO_3)_2$ solution in test tube 2. Mix thoroughly, and record your observations in the table on the Data Sheet. Complete the last two columns of the table to indicate if a reaction occurred, etc.

11. Add 3 drops of 0.10 M Na_2SO_4 solution to the $Ba(NO_3)_2$ solution in test tube 3 and mix thoroughly. Record your observations and complete the last two columns in the table on the Data Sheet.

12. Add 5 drops of saturated $NaC_2H_3O_2$ to the solution in test tube 3. Record your observations and complete the appropriate sections of the table on the Data Sheet.

13. Discard the contents of test tubes 1, 2, and 3 into your waste beaker. Rinse each test tube and the graduated cylinder twice with 5 mL portions of tap water, and twice with 5 mL portions of distilled water. Add these rinse solutions to the waste beaker.

C. Reactions of Pb^{2+} Ion

14. Obtain 8 mL of 0.10 M $Pb(NO_3)_2$ solution in a clean, dry graduated cylinder. Pour about 2 mL into each of the numbered test tubes, and pour the remaining 2 mL into the test tube labeled Pb^{2+}.

15. Add 3 drops of 0.10 M KSCN solution to the $Pb(NO_3)_2$ solution in test tube 1. Mix the solutions in the test tube thoroughly. Record your observations in the table on the Data Sheet, and indicate if a reaction occurred (Y or N). If a reaction did occur, write the chemical reaction in the last column.

16. Add 15 drops of the 1.0 M HCl to the $Pb(NO_3)_2$ solution in test tube 2. Mix thoroughly, and record your observations in the table on the Data Sheet. Complete the last two columns of the table to indicate if a reaction occurred, etc.

17. Add 3 drops of 0.10 M Na_2SO_4 solution to the $Pb(NO_3)_2$ solution in test tube 3 and mix thoroughly. Record your observations and complete the last two columns in the table on the Data Sheet.

18. Add 5 drops of saturated $NaC_2H_3O_2$ to the solution in test tube 3. Record your observations and complete the appropriate sections of the table on the Data Sheet.

19. Discard the contents of test tubes 1, 2, and 3 into your waste beaker. Rinse each test tube and the graduated cylinder twice with 5 mL portions of tap water, and twice with 5 mL portions of distilled water. Add these rinse solutions to the waste beaker. Transfer the

contents of your waste beaker into the appropriate container as directed by your lab instructor.

D. Identifying Ions in a Mixture

20. Pour the 2 mL of $Pb(NO_3)_2$ solution in the Pb^{2+} test tube and the 2 mL of $Ba(NO_3)_2$ solution in the Ba^{2+} test tube into the Fe^{3+} test tube. Mix the contents of the Fe^{3+} test tube thoroughly.

21. Pour 2 mL of the mixture in the Fe^{3+} test tube into test tubes 1, 2, and 3.

22. Add 3 drops of 0.10 M KSCN solution to the mixture in test tube 1. Mix the solutions in the test tube thoroughly. Record your observations and complete the appropriate entries in the table on the Data Sheet.

23. Add 15 drops of the 1.0 M HCl to the mixture in test tube 2, and mix thoroughly. Record your observations and complete the appropriate entries in the table on the Data Sheet.

24. Add 3 drops of 0.10 M Na_2SO_4 solution to the mixture in test tube 3 and mix thoroughly. Record your observations and complete the appropriate entries in the table on the Data Sheet.

25. Add 5 drops of saturated $NaC_2H_3O_2$ to the solution in test tube 3. Record your observations and complete the appropriate sections of the table on the Data Sheet.

26. Discard the contents of test tubes 1, 2, and 3 into your waste beaker. Rinse each test tube twice with 5 mL portions of tap water, and twice with 5 mL portions of distilled water. Add these rinse solutions to the waste beaker.

E. Qualitative Analysis of Unknown Mixture

27. Obtain 6 mL of the unknown mixture assigned by your lab instructor. Record the ID for your unknown solution on the Data Sheet.

28. Pour 2 mL of the unknown mixture into test tubes 1, 2, and 3.

29. Add 3 drops of 0.10 M KSCN solution to the mixture in test tube 1. Mix the solutions in the test tube thoroughly. Record your observations and complete the appropriate entries in the table on the Data Sheet.

30. Add 15 drops of the 1.0 M HCl to the mixture in test tube 2, and mix thoroughly. Record your observations and complete the appropriate entries in the table on the Data Sheet.

31. Add 3 drops of 0.10 M Na_2SO_4 solution to the mixture in test tube 3 and mix thoroughly. Record your observations and complete the appropriate entries in the table on the Data Sheet.

32. Add 5 drops of saturated $NaC_2H_3O_2$ to the solution in test tube 3. Record your observations and complete the appropriate sections of the table on the Data Sheet.

33. Discard the contents of test tubes 1, 2, and 3 into your waste beaker. Rinse each test tube twice with 5 mL portions of tap water, and twice with 5 mL portions of distilled water. Add these rinse solutions to the waste beaker. Transfer the contents of the waste beaker into the appropriate container as directed by your lab instructor.

34. **Wash your hands thoroughly with soap before leaving the laboratory.**

Data Sheet

Test Solution	Reagent Added	Observations	Reaction? (Y/N)	Chemical Equation
$Fe(NO_3)_3$	KSCN			
	HCl			
	Na_2SO_4			
$Ba(NO_3)_2$	KSCN			
	HCl			
	Na_2SO_4			
$Ba(NO_3)_2$ + Na_2SO_4	$NaC_2H_3O_2$			
$Pb(NO_3)_2$	KSCN			
	HCl			
	Na_2SO_4			
$Pb(NO_3)_2$ + Na_2SO_4	$NaC_2H_3O_2$			

Data Sheet (con't.)

Test Solution	Reagent Added	Observations	Reaction? (Y/N)	Ions Present?
Mixture (all 3 cations)	KSCN			
	HCl			
	Na_2SO_4			
Mix + Na_2SO_4	$NaC_2H_3O_2$			

Unknown ID:______________________

Test Solution	Reagent Added	Observations	Reaction? (Y/N)	Ions Present?
Unknown	KSCN			
	HCl			
	Na_2SO_4			
Unknown + Na_2SO_4	$NaC_2H_3O_2$			

Conclusion: Ions present in the unknown solution : ____________________________________

Post-Lab Questions

A student studied some reactions involving Pb^{2+}, Cu^{2+} and Ni^{2+} ions. First the student reacted the individual metal cations with 1 M HCl and 1 M NaOH solutions. The student then added some NH_3 to each of the cation-NaOH reaction mixtures. The observations for each test were recorded and are presented in the table below:

Test Solution	Reagent Added	Observations
$Pb(NO_3)_2$	HCl	White precipitate forms; precipitate dissolves upon addition of more HCl.
	NaOH	White precipitate forms.
$Pb(NO_3)_2$ + NaOH	NH_3	No change observed.
$Cu(NO_3)_2$	HCl	No reaction.
	NaOH	Blue precipitate forms.
$Cu(NO_3)_2$ + NaOH	NH_3	Blue precipitate dissolves, forming clear blue solution.
$Ni(NO_3)_2$	HCl	No reaction.
	NaOH	White precipitate forms.
$Ni(NO_3)_2$ + NaOH	NH_3	White precipitate dissolves, forming violet solution.

1. Based on the student observations, describe a procedure to:

a) Confirm the presence of Pb^{2+} in a mixture of Pb^{2+} and Cu^{2+} ions.

b) Confirm the presence of Ni^{2+} in a mixture of Pb^{2+} and Ni^{2+} ions.

2. Would it be possible to confirm the presence of Cu^{2+} or Ni^{2+} in a mixture of these two ions? Why or why not?

3. The qualitative analysis scheme in this exercise involved adding reagents to confirm the presence of cations, specifically, Ba^{2+}, Pb^{2+}, and Fe^{3+}. Could this or a similar procedure be used for the qualitative analysis of anions? Review your observations and suggest a procedure that could be used to confirm the presence of the following anions. For each case, write the net ionic equation for the reaction involved.

a) Chloride (Cl^-):

b) Sulfate (SO_4^{2-}):