General Chemistry II Laboratory

Experiment #2 Inorganic Qualitative Analysis

Separation and Characterization of Group A Cations

Introduction: Inorganic qualitative analysis is the unambiguous identification of cations (and/or anions) which are present in a given solution. Unique tests for all ions in the possible presence of all others are virtually impossible to devise. Many tests give similar results with different cations. But if a solution is treated to separate ions into smaller groups, identification is simplified.

The most common way to subdivide cations into smaller groups is by selective precipitation, in which a small group of cations is precipitated chemically. The precipitate can then be physically separated from the remaining cations in solution by centrifuging. The precipitate (insoluble solid) settles out and the solution (supernatant liquid) is decanted into another container. In this way the initial large group can be separated into smaller and smaller groups until a definitive test can be performed to verify the presence or absence of each specific cation.

It is important to realize that many chemical reactions do not go to completion. The extent to which a reaction occurs depends on the magnitude of the equilibrium constant, K_{sp} for the reaction and the concentrations of reagents present. Equilibria can be shifted by adding or removing reagents and by altering the physical conditions in accordance with Le Châtelier's principle. In this analysis scheme, you will use various reagents to force precipitation to occur, dissolve sparingly soluble compounds or complex particular ions so they will not interfere with tests for other ions.

There are several ways to classify metal ions according to the solubility of the compounds they form with various anions. We will use an abbreviated classification of ions into two groups called A and B. You will analyze an unknown solution containing from three to six of the cations in Group A (Bi^{+3}, Fe^{+3}, Mn^{+2}) and Group B (Al^{+3}, Cr^{+3}, Sn^{+4}) during the next two laboratory periods. The ions in an combined unknown solution will be separated into the two groups and then each portion will be analyzed for the cations present.

A useful way of tabulating qualitative analysis results is with a divided page. The left column lists the test procedures, the center column the test results, and the right column the conclusions drawn from the test results. The technique is illustrated below for a solution of known ions and for a hypothetical unknown solution.

	Test	Result	Conclusions
1	Add NH_3 at pH 10 to known and unknown	Red precipitate formed in known and unknown	Possible Group A and/or Group B cations present n both
2	Add NaOH and H_2O_2 to known and unknown	Half of precipitate in known and unknown dissolves	Possible Group A and B cations in known and unknown
3	Add hot HCl to known and unknown	Precipitate in both known and unknown dissolves	Mn^{+2}, Bi^{+3} and Sn^{+2} possible in known and unknown
4	Add H_2O_2 and BiO_3^{1-} to known and unknown	Purple solution in known solution while unknown remains colorless	Mn^{+4} present in known No Mn^{+4} present in unknown

Your initial unknown will contain from three to six cations from Groups A and B. You will separate the two groups and analyze Group A this week. At the next lab period, you will analyze Group B.

Groups A and B cations react with NH_3 (at pH 10) to precipitate as hydroxides or oxides. Group A cations react in ammonia solution according to the equations:

$$Bi^{+3}(aq) + 3NH_3(aq) + 3H_2O(l) \rightarrow Bi(OH)_3(s)\ (white) + 3\ NH_4^{+1}(aq)$$

$$Fe^{+3}(aq) + 3NH_3(aq) + 3H_2O(l) \rightarrow Fe(OH)_3(s)\ (red\text{-}brown) + NH_4^{+1}(aq)$$

$$Mn^{+2}(aq) + 2NH_3(aq) + 2H_2O(l) \rightarrow Mn(OH)_2(s)\ (pale\ pink) + 2\ NH_4^{+1}(aq)$$

Group B cations precipitate as $Al(OH)_3$, $Cr(OH)_3$ and SnO_2.

$$Al^{+3}(aq) + 3NH_3(aq) + 3H_2O(l) \rightarrow Al(OH)_3(s)\ (white) + 3\ NH_4^{+1}(aq)$$

$$Cr^{+3}(aq) + 3NH_3(aq) + 3H_2O(l) \rightarrow Cr(OH)_3(s)\ (green) + 3\ NH_4^{+1}(aq)$$

$$Sn^{+4}(aq) + 2H_2O(l) + 4NH_3(aq) \rightarrow SnO(s)\ (white) + 4\ NH_4^{+1}(aq)$$

On addition of NaOH and H_2O_2, to the mixed group precipitate, the Group B cations will dissolve while the Group A cations remain as solids. At this point, the Group A cations can be separated physically from Group B by centrifuging and decanting. You will save the precipitate containing the Group A ions for analysis in the first week. You will save the supernatant liquid containing the Group B cations for analysis next week. $Bi(OH)_3$ and $Fe(OH)_3$ do not react further with either NaOH or H_2O_2, but $Mn(OH)_2$ is converted to MnO_2 as shown in the equation below.

$$Mn(OH)_2(s) + H_2O_2(aq) \rightarrow MnO_2(s) + 2H_2O(l)$$

The precipitate of Group A cations is dissolved in hot HCl to give a solution containing Bi^{+3}, Fe^{+3}, and Mn^{+4} ions. Some Mn^{+4} may be converted to Mn^{+2} but this will have no effect on the confirmation of manganese. The tests for each of these three cations can be carried out without any further separation. A separate aliquot of this acidic solution will be used for each of the following tests.

Manganese(II) Ion: The Mn^{+4} ion is treated with H_2O_2 to convert it to Mn^{+2}. The Mn(II) ion is treated with bismuthate ion (BiO_3^{-1}) to form the purple permanganate ion. These reactions are shown in the following equations. The appearance of the purple permanganate color confirms Mn^{+2}.

$$Mn^{+4}(aq) + H_2O_2(aq) \rightarrow Mn^{+2}(aq) + O_2(aq) + 2H^{+l}(aq)$$

$$14H^{+l}(aq) + 2Mn^{+2}(aq) + 5BiO_3^{-1}(aq) \rightarrow 5Bi^{+3}(aq) + 7H_2O(l) + 2MnO_4^{-1}(aq)\ (purple)$$

Bismuth Ion: In the second portion of solution, Bi^{+3} ion, present as $Bi(OH)_3$, is reduced to metallic bismuth (Bi^o) by Sn^{+2}. This reaction occurs in basic solution in which Sn(II) exists as the $Sn(OH)_3^{-1}$ ion. The appearance of a black precipitate confirms Bi^{+3}. The reactions are as follows:

$$Bi^{+3}(aq) + 30H^{-1}(aq) \rightarrow Bi(OH)_3(s)$$

$$Sn^{+2}(aq) + OH^{-1}(aq) \rightarrow Sn(OH)_3^{-1}(aq)$$

$$2Bi(OH)_3(s) + 3Sn(OH)_3^{-1}(aq) + 3\ OH^{-1}(aq) \rightarrow 2Bi(s) + 3Sn(OH)_6^{-2}(aq)\ \text{(black)}$$

Iron(III) Ion The third portion of the solution is tested for the ferric ion by adding KSCN solution. If Fe^{+3} is present, the red-brown complex $FeSCN^{+2}(aq)$ forms. This color confirms the presence of Fe^{+3}.

$$Fe^{+3}(aq) + SCN^{-1}(aq) \rightarrow FeSCN^{+2}(aq)\ \text{(red-brown)}$$

Waste Disposal: In all laboratory procedures, proper disposal of waste is an important environmental and legal issue. CCRI's policy is not to pour *any* chemicals down the drain. During analysis of Group A and Group B cations, all waste must go into the heavy metal waste collection container. Chromium found in Group A has a 0.5 ppm discharge limit. One act of careless disposal could exceed this value and put CCRI at risk for a sewer authority citation. The situation is even more critical in Group B analysis. Mercury has a discharge limit of only 30 parts per *billion*. Extreme care is needed to keep even the smallest trace of this dangerous pollutant out of the sewer system.

The best procedure is to collect all solid and liquid waste and the rinse water from your glassware in a marked beaker at your bench. At the end of the lab empty the beaker contents and rinse the beaker into the container marked "Heavy Metal Waste". Do not wash anything in the sink until all chemical residues have been transferred to the heavy metal waste collection container.

Experimental Your initial unknown will contain from one to six cations from Groups A and B. The known solution will contain all six cations for comparison purposes.

Simultaneously follow the experimental procedure with the known mixture (containing all three cations) and your unknown mixture (which may contain one, two, or all three of the cations). Then you can compare the known with your unknown solution. Be sure to label your test tubes to prevent mixups. Collect all discarded solids and solutions in a beaker and dispose of them in the heavy metal waste container.

Place 20 drops of your unknown solution and 20 drops of the standard Group A cations into two separate labeled test tubes. Treat both test tubes identically and record your observations.

Add 6M NH_3 dropwise, with stirring, to bring the pH to between 9 to 10. Check the pH wide range (1-12) pH paper. Stir thoroughly before testing the pH. Use a stirring rod to transfer one drop of the solution to the pH paper. Do not dip the pH paper into the test solution. Centrifuge the solution for two minutes and decant. Discard the supernatant liquids in the heavy metal waste collection container.

Add 20 drops of 6M NaOH and 4 drops of 3% H_2O_2 to the precipitate, stir thoroughly, and let the solution sit for two minutes. Centrifuge for two minutes and decant. Label and put aside the supernatant liquids from your known and unknown solutions for analysis of the Group B cations next week.

Add 4 mL of distilled water to the Group A precipitate and heat in a hot water bath for 10 minutes to destroy any excess peroxide: Centrifuge for two minutes. Decant the supernatant liquid and discard it. Wash the precipitate with 4 mL of distilled water and discard the wash liquid.

Add 20 drops of 6M HCl to the precipitate, stir, and heat for two minutes in the hot water bath. Add 4 drops of 3% hydrogen peroxide to the solution. Let the solution sit for 30 seconds, then heat the solution for two minutes in the water bath. Cool to room temperature and perform the following tests.

Confirmation of Mn^{+2} Ion: Place 8 drops of the test solution into a clean test tube. Add several small portions of solid $NaBiO_3$ with stirring until no further reaction occurs. If the solution is cloudy, centrifuge, decant the supernatant liquid and note its color. A pink to purple supernatant liquid confirms the presence of Mn^{+2}.

Confirmation of Bi^{+3} Ion: Place four drops of the test solution in a clean test tube. Add 6 drops of 6M NaOH and then a small quantity of solid $SnC1_2$. The immediate appearance of a black precipitate confirms the presence of Bi^{+3}.

Confirmation of Fe^{+3} Ion: Place 12 drops of the test solution into a clean test tube. Add 6 drops of 0.1M KSCN solution. The appearance of a red-brown solution confirms the presence of Fe^{+3}.

Name:_____ Section No:_____

Qualitative Analysis Report
Group A Cations
Data Page for Known Solution

Test	Result	Conclusion

Name:_____ Section No:_____

Qualitative Analysis Report
Group A Cations
Data Page for Unknown Solution

Unknown No._____

Test	Result	Conclusion

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Report for Experiment #2, Inorganic Qualitative Analysis

Separation and Characterization of Group A Cations

Name:_____ Section No:_____

Unknown No._____

1. What Group A cation(s) are present in your unknown ?

_____ _____ _____ (15 points)

2. Draw a flow diagram showing the steps and products you found in the analysis of your unknown. (5 points)

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Prestudy for Experiment #2 Inorganic Qualitative Analysis

Separation and Characterization of Group A Cations

Name:_____ Section No:_____

An unknown solution containing only Group A cations is treated according to the lab procedure discussed. At each stage below, state what cations may be present, which are confirmed present, and which are absent.

(a) The solution is treated with NH_3 until the pH is 9. A colored precipitate is formed which is insoluble in NaOH-H_2O_2 but soluble in HCl. (2 points)

(b) Four drops of the solution from step (a) are treated with $NaBiO_3$. A clear purple solution forms. (2 points)

(c) Two drops of the solution from step (a) are treated with 6M NaOH and solid $SnC1_2$. A black solid forms. (2 points)

(d) A portion of the solution from step (a) is treated with KSCN. A clear solution results. (2 points)