

## Group A Cation Analysis

### Inorganic Qualitative Analysis

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.

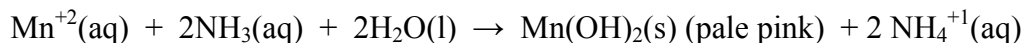
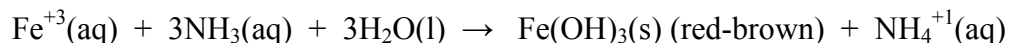
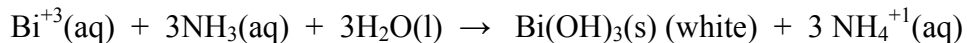
There are several ways to classify metal ions according to the solubility of the compounds they form with various anions. We will use an abbreviated classification of ions into two groups called A and B. You will analyze an unknown solution containing from three to six of the cations in Group A ( $\text{Bi}^{+3}$ ,  $\text{Fe}^{+3}$ ,  $\text{Mn}^{+2}$ ) and Group B ( $\text{Al}^{+3}$ ,  $\text{Cr}^{+3}$ ,  $\text{Sn}^{+4}$ ) 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.

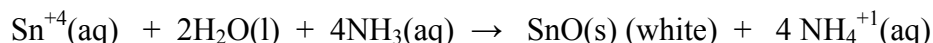
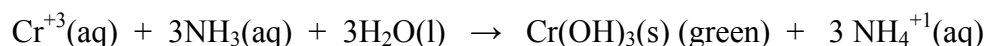
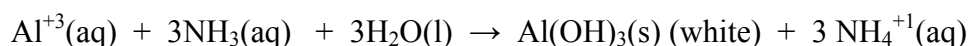
	Test	Result	Conclusions
1	Add $\text{NH}_3$ at pH 10 to known and unknown	Red precipitate formed in known and unknown	Possible Group A and/or Group B cations present in both
2	Add $\text{NaOH}$ and $\text{H}_2\text{O}_2$ to known and unknown	Half of precipitate in known and unknown dissolves	Possible Group A and B cations in known and unknown
3	Add hot $\text{HCl}$ to known and unknown	Precipitate in both known and unknown dissolves	$\text{Mn}^{+2}$ , $\text{Bi}^{+3}$ and $\text{Sn}^{+2}$ possible in known and unknown
4	Add $\text{H}_2\text{O}_2$ and $\text{BiO}_3^{1-}$ to known and unknown	Purple solution in known solution while unknown remains colorless	$\text{Mn}^{+4}$ present in known No $\text{Mn}^{+4}$ 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.

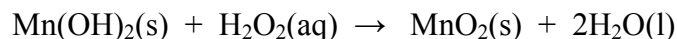
Groups A and B cations react with  $\text{NH}_3$  (at pH 10) to precipitate as hydroxides or oxides. Group A cations react in ammonia solution according to the equations:



Group B cations precipitate as  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$  and  $\text{SnO}_2$ .



On addition of  $\text{NaOH}$  and  $\text{H}_2\text{O}_2$ , 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.  $\text{Bi}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  do not react further with either  $\text{NaOH}$  or  $\text{H}_2\text{O}_2$ , but  $\text{Mn}(\text{OH})_2$  is converted to  $\text{MnO}_2$  as shown in the equation below.

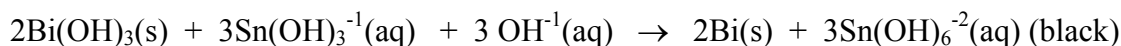
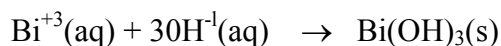


The precipitate of Group A cations is dissolved in hot  $\text{HCl}$  to give a solution containing  $\text{Bi}^{+3}$ ,  $\text{Fe}^{+3}$ , and  $\text{Mn}^{+4}$  ions. Some  $\text{Mn}^{+4}$  may be converted to  $\text{Mn}^{+2}$  but this will have no effect on the confirmation of manganese. The tests 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  $\text{Mn}^{+4}$  ion is treated with  $\text{H}_2\text{O}_2$  to convert it to  $\text{Mn}^{+2}$ . The  $\text{Mn}(\text{II})$  ion is treated with bismuthate ion ( $\text{BiO}_3^{-1}$ ) to form the purple permanganate ion. These reactions are shown in the following equations. The appearance of the purple permanganate color confirms  $\text{Mn}^{+2}$ .



**Bismuth Ion:** In the second portion of solution,  $\text{Bi}^{+3}$  ion, present as  $\text{Bi}(\text{OH})_3$ , is reduced to metallic bismuth ( $\text{Bi}^0$ ) by  $\text{Sn}^{+2}$ . This reaction occurs in basic solution in which  $\text{Sn}(\text{II})$  exists as the  $\text{Sn}(\text{OH})_3^{-1}$  ion. The appearance of a black precipitate confirms  $\text{Bi}^{+3}$ . The reactions are as follows:



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



**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  $\text{NH}_3$  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%  $\text{H}_2\text{O}_2$  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  $\text{Mn}^{+2}$  Ion:** Place 8 drops of the test solution into a clean test tube. Add several small portions of solid  $\text{NaBiO}_3$  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  $\text{Mn}^{+2}$ .

**Confirmation of  $\text{Bi}^{+3}$  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  $\text{SnCl}_2$ . The immediate appearance of a black precipitate confirms the presence of  $\text{Bi}^{+3}$ .

**Confirmation of  $\text{Fe}^{+3}$  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  $\text{Fe}^{+3}$ .

Name: \_\_\_\_\_

**Qualitative Analysis of Group A Cations**

**Data Page for Known Solution**

<b>Test</b>	<b>Result</b>	<b>Conclusion</b>

Name: \_\_\_\_\_

## Qualitative Analysis of Group A Cations

### Data Page for Unknown Solution

Unknown No. \_\_\_\_\_

<b>Test</b>	<b>Result</b>	<b>Conclusion</b>

Name: \_\_\_\_\_

### Results of Group A Cations

Unknown No. \_\_\_\_\_

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

\_\_\_\_\_

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

Name: \_\_\_\_\_

## Group A Cation Analysis

### Prestudy

An unknown solution containing Group A and Group B cations is treated according to the lab procedure. At each stage below, state what each test tells you about which cations may be present, which are confirmed present, which are absent, and why.

(a) The solution is treated with  $\text{NH}_3$  until the pH is 9 to give a colored precipitate. The precipitate was treated with  $\text{NaOH-H}_2\text{O}_2$  and the mixture centrifuged and separated to give a yellow solution and a precipitate. The yellow solution was saved for the Group B cation analysis. The remaining precipitate was dissolved in  $\text{HCl}$  and the clear solution analyzed as follows.

(b) Four drops of the clear solution from step (a) are treated with  $\text{NaBiO}_3$  to give a purple solution.

(c) Two drops of the solution from step (a) are treated with 6M  $\text{NaOH}$  and solid  $\text{SnCl}_2$  to give a black solid.

(d) A portion of the solution from step (a) is treated with  $\text{KSCN}$  and the solution remains clear.