

Abbreviated Qualitative-Analysis Scheme

EXPERIMENT

29

Ag^+ , Pb^{2+} , Hg_2^{2+} , Cu^{2+} , Bi^{3+} , Sn^{4+} , Fe^{3+} , Mn^{2+} , Ni^{2+} , Al^{3+} , Ba^{2+} , NH_4^+ , Na^+ .

CATIONS:

SO_4^{2-} , NO_3^- , CO_3^{2-} , Cl^- , Br^- , I^- , CrO_4^{2-} , PO_4^{3-} , S^{2-} , SO_3^{2-} .

ANIONS:

To become acquainted with the chemistry of several elements and the principles of qualitative analysis.

OBJECTIVE

small test tubes (12)
centrifuge
unknown cation solution
unknown anion salt (as solid mixture)
casserole
evaporating dish
litmus
droppers (6)
Nichrome wire (10 cm)
Bunsen burner and hose
6 M $\text{HC}_2\text{H}_3\text{O}_2$
12 M HCl
6 M HCl
2 M HCl
0.2 M BaCl_2
mineral oil
 Cl_2 -water
diethyl ether
dimethylglyoxime 1 percent^d

6 M HNO_3
3 M HNO_3
6 M H_2SO_4
18 M H_2SO_4
15 M NH_3
6 M NH_3
 $\text{Ba}(\text{OH})_2$, saturated solution
6 M NaOH
aluminum, 0.1 percent^a
aluminum wire, 26 guage
1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$
2 M NH_4Cl
 $(\text{NH}_4)_2\text{MoO}_4$ ^b
0.2 m SnCl_2 (Freshly Prepared)
 $(\text{NH}_4)_2\text{S}$ ^c
1 M K_2CrO_4
1 M $\text{K}_2\text{C}_2\text{O}_4$
0.2 M KNO_2
0.2 M KSCN
0.1 M AgNO_3

APPARATUS
AND CHEMICALS

^a One gram of ammonium aurintricarboxylic acid in 1 L H_2O .

^b Dissolve 20 g of MoO_3 in a mixture of 60 mL of distilled water and 30 mL of 15 M NH_3 . Add this solution slowly, with constant stirring, to a mixture of 230 mL of water and 100 mL of 16 M HNO_3 .

^c Add 1 volume of reagent-grade ammonium sulfide liquid to two volumes of water or saturate 5 M NH_3 with H_2S .

^d In 95% ethyl alcohol solution.

| | |
|----------------------------------------------------------------------|------------------------------------------------------|
| ethyl alcohol, 95 percent | NaBiO ₃ , solid |
| 0.2 M Fe(NO ₃) ₂ | Na ₂ CO ₃ , saturated solution |
| 0.2 M FeSO ₄ | Na ₂ O ₂ , solid |
| H ₂ O ₂ , 3 percent | starch solution |
| 0.2 M Pb(C ₂ H ₃ O ₂) ₂ | 1 M thioacetamide |
| 0.1 M MnCl ₂ | Zn, granulated |
| 0.1 M HgCl ₂ | Group 1, 2, 3, and 4 known solutions |
| 0.1 M Hg(C ₂ H ₃ O ₂) ₂ | Solid sodium salt anion knowns |
| 16 M HNO ₃ | |

ALL SOLUTIONS SHOULD BE PROVIDED IN DROPPER BOTTLES

CATIONS

Discussion

Qualitative analysis is concerned with the identification of the constituents contained in a sample of unknown composition. Inorganic qualitative analysis deals with the detection and identification of the elements that are present in a sample of material. Frequently this is accomplished by making an aqueous solution of the sample and then determining which cations and anions are present on the basis of chemical and physical properties. In this experiment, you will be exposed to some of the chemistry of 14 cations (Ag⁺, Pb²⁺, Hg₂²⁺, Cu²⁺, Bi³⁺, Sn⁴⁺, Fe³⁺, Mn²⁺, Ni²⁺, Al³⁺, Ba²⁺, Ca²⁺, NH₄⁺, Na⁺) and 10 anions (CrO₄²⁻, PO₄³⁻, S²⁻, SO₃²⁻, SO₄²⁻, NO₃⁻, Cl⁻, Br⁻, I⁻, CO₃²⁻), and you will learn how to test for their presence or absence. Because there are many elements and ions other than those which we shall consider, we call this experiment an "abbreviated" qualitative-analysis scheme.

If a sample contains only a single cation (or anion), its identification is a fairly simple and straightforward process, as you may have witnessed in Experiment 28. However, even in this instance additional confirmatory tests are sometimes required to distinguish between two cations (or anions) that have similar chemical properties. The detection of a particular ion in a sample that contains several ions is somewhat more difficult, because the presence of the other ions may interfere with the test. For example, if you are testing for Ba²⁺ with K₂CrO₄ and obtain a yellow precipitate you may draw an erroneous conclusion because if Pb²⁺ is present, it also will form a yellow precipitate. Thus lead ions interfere with this test for barium ions. This problem can be circumvented by precipitating the lead as PbS with H₂S first, thereby removing the lead ions from solution prior to testing for Ba²⁺.

The successful analysis of a mixture containing 14 or more cations centers upon the systematic separation of the ions into groups containing only a few ions. It is a much simpler task to work with 2 or 3 ions than with 14 or more. Ultimately, the separation of cations depends upon the difference in their tendencies to form precipitates, to form complex ions, or to exhibit amphoterism.

The chart in Figure 29.1 illustrates how the 14 cations you will study are separated into groups. Note that only 4 of the 14 cations are colored: Fe³⁺ (rust to yellow), Cu²⁺ (blue), Mn²⁺ (very faint pink), and Ni²⁺ (green). Therefore a preliminary examination of an unknown that can contain any of the 14 cations under consideration yields valuable information. If the solution is colorless, you

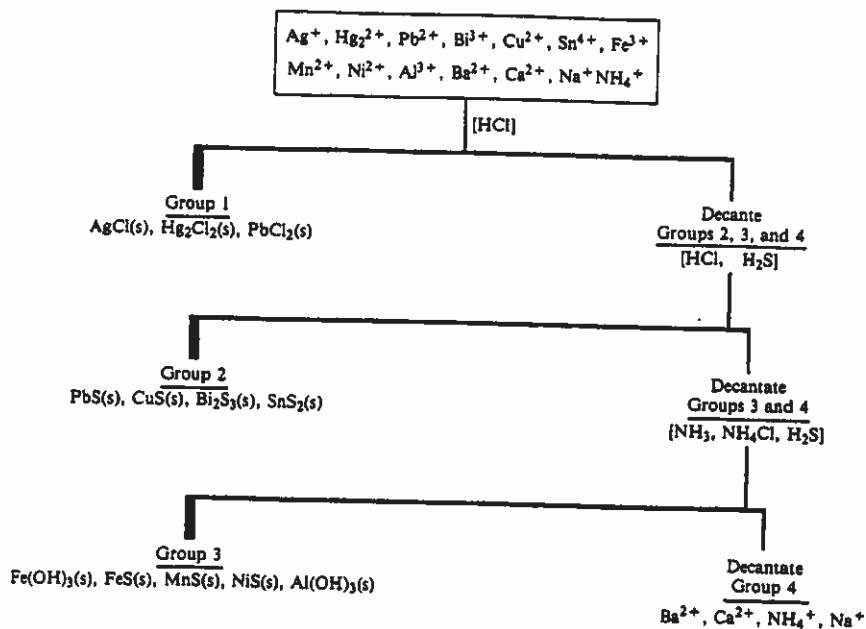


Figure 29.1 Flow chart for group separation.

know immediately that iron, copper, and nickel are absent. You are to take advantage of all clues that will aid you in identifying ions. However, in your role as a detective in identifying ions, be aware that clues can sometimes be misleading. For example, if Fe^{3+} and Ni^{2+} are present together, what color would you expect this mixture to display? Would the color depend upon the proportions of Fe^{3+} and Ni^{2+} present? Could you assign a definite color to such a mixture? The extremely faint pink color of Mn^{2+} may not be discerned unless you carefully examine the solution, and the presence of any of the other colored ions will definitely mask its color.

The group separation chart (Figure 29.1) shows that silver, mercury(I), and lead can be separated from all the other cations as insoluble chlorides by the addition of hydrochloric acid. Addition of hydrogen sulfide and hydrochloric acid to the decantate results in the precipitation of the sulfides of lead, copper, bismuth, and tin(IV). The reason why lead appears in both groups 1 and 2 is explained by the chemistry of these group cations. In order to derive any benefit from this exercise you must become thoroughly familiar with the group-separation chart in Figure 29.1. When you work with the four groups, you will see additional separation charts or flow schemes for the individual groups. Become familiar with these also. It is important to keep in mind what cations you are working with in each group. Know their formulas and charges and become familiar with how they are separated and identified.

You will analyze four known solutions, one for each group. Each of these solutions will contain all of the cations in the group you are studying. Then you will analyze a group unknown for each of the groups. Your instructor may tell you to analyze the known and unknown side by side. If you do, be careful not to mix up your test tubes! As you proceed with your analysis, record on your report sheets the reagents used in each step, your observations, and the equations for each precipitation reaction. After completing the four groups, you will analyze a general cation unknown that may contain any number of the 14 ions studied.

PART A

GROUP 1 CATIONS: Pb²⁺, Ag⁺, Hg₂²⁺

Chemistry of Group 1 Cations

Because the chlorides of Pb²⁺, Ag⁺, and Hg₂²⁺ are insoluble, they may be precipitated and separated from the cations of groups 2, 3, and 4 by the addition of HCl. The following equations represent the reactions that occur:



A slight excess of HCl is used to ensure complete precipitation of the cations and to reduce the solubility of the chlorides by the common-ion effect. However, a large excess of chloride must be avoided, because both AgCl and PbCl₂ tend to dissolve by forming soluble complex anions:



PbCl₂ is appreciably more soluble than either AgCl or Hg₂Cl₂. Thus, even when PbCl₂ precipitates, a significant amount of Pb²⁺ remains in solution and is subsequently precipitated with the group 2 cations as the sulfide PbS. Because of its solubility, Pb²⁺ sometimes does not precipitate as the chloride, because either its concentration is too small or the solution is too warm.

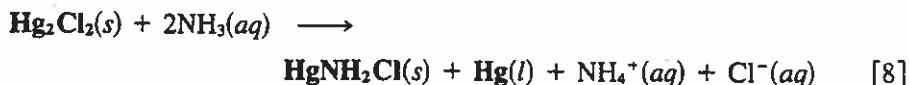
Lead Lead chloride is much more soluble in hot water than in cold. It is separated from the other two insoluble chlorides by dissolving it in hot water. The presence of Pb²⁺ is confirmed by the formation of a yellow precipitate, PbCrO₄, upon the addition of K₂CrO₄:



Mercury(I) Silver chloride is separated from Hg₂Cl₂ by the addition of aqueous NH₃. Silver chloride dissolves because Ag⁺ forms a soluble complex cation with NH₃:



Mercury(I) chloride reacts with aqueous ammonia in a disproportionation reaction to form a dark gray precipitate:



Although HgNH₂Cl is white, the precipitate appears dark gray because of a colloidal dispersion of Hg(l).

Silver To verify the presence of Ag⁺, the supernatant liquid from the last reaction is acidified and AgCl reprecipitates if Ag⁺ is present. The acid decom-

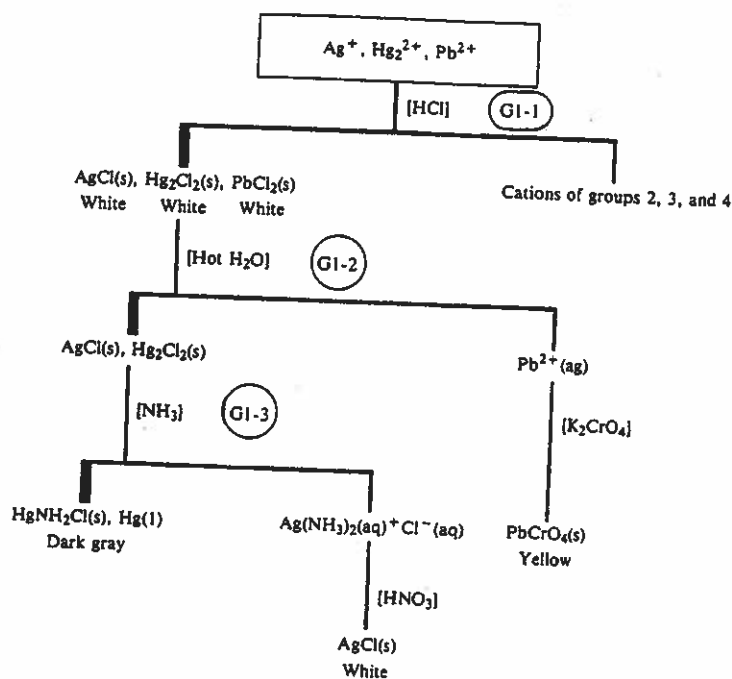
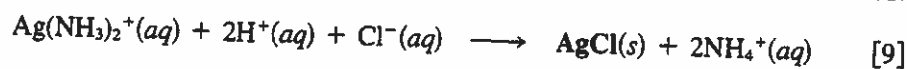


Figure 29.2 Group 1 flow scheme. Procedure numbers are given in the circles.

poses $\text{Ag}(\text{NH}_3)_2^+$ by neutralizing NH_3 to form NH_4^+ . It is necessary that the solution be acidic, or else the AgCl will not precipitate and Ag^+ can be missed.



The flow chart in Figure 29.2 shows how the group 1 cations are separated and identified. *You should become very familiar with it and consult it often as you perform your analysis.*

First you will analyze a known that contains all three cations of group 1. Record on your report sheet the reagents used in each step, your observations, and the equation for each precipitation reaction. After completing the analysis of a known, obtain an unknown. Follow the same procedures as with the known. Also record conclusions regarding the presence or absence of all cations. *Before beginning this experiment review the techniques used in qualitative analysis found in Appendix J: centrifugation, heating solutions, washing precipitates, and testing acidity.*

(G1-1) Precipitation of Group 1 Cations

Measure out 10 drops (0.5 mL) of the test solution or the unknown into a small (10 mm × 75 mm) test tube. Add 4 drops of 6 M HCl, stir thoroughly, and then centrifuge. Test for completeness of precipitation by adding 1 drop of 6 M HCl to the clear supernate. If the supernate turns cloudy, this shows that not all of the group 1 cations have precipitated; add another 2 drops of 6 M HCl, stir, and centrifuge. Repeat this process until no more precipitate forms. All of the group 1 cations must be precipitated or else they will slip through and interfere with subsequent group analysis. If a general unknown is being analyzed, de-

PROCEDURE

cant the supernate into a clean test tube and save it for analysis of group 2 cations; otherwise, discard it. Wash the precipitate by adding 5 drops of cold distilled water and stirring. Centrifuge and add the liquid to the supernate. Why is the precipitate washed? See Appendix J.

G1-2 Separation and Identification of Pb^{2+}

Add 15 drops of distilled water to the precipitate and place the test tube in a hot-water bath. Stir using a stirring rod and heat for 1 min or longer. Quickly centrifuge and decant the hot supernate into a clean test tube. Repeat this procedure two more times, combining the supernates, which should contain Pb^{2+} if it is present. Save the precipitate for procedure G1-3. Add 3 drops of 1 M K_2CrO_4 to the supernate. The formation of a yellow precipitate, PbCrO_4 , confirms the presence of Pb^{2+} .

G1-3 Separation and Identification of Ag^+ and Hg_2^{2+}

Add 10 drops of 6 M NH_3 to the precipitate from step G1-2. The formation of a dark gray precipitate indicates the presence of mercury. Centrifuge and decant the clear supernate into a clean test tube. Add 20 drops of 6 M HNO_3 to the decantate. Stir the solution and test its acidity. Continue to add HNO_3 dropwise until the solution is acidic. A white cloudiness confirms the presence of Ag^+ .

REVIEW QUESTIONS

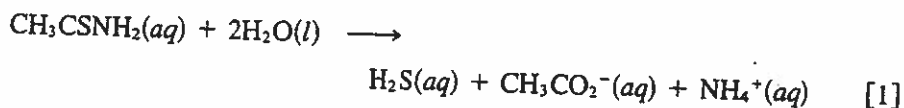
Before beginning Part A of this experiment in the laboratory, you should be able to answer the following questions:

1. What are the symbols and charges of the group 1 cations?
2. Which chloride salt is insoluble in cold water but soluble in hot water?
3. Which chloride salt dissolves in aqueous NH_3 ?
4. How could you distinguish:
 - (a) BaCl_2 from AgCl ?
 - (b) HNO_3 from HCl ?
5. Complete and balance the following equations:
 - (a) $\text{AgCl}(s) + \text{NH}_3(aq) \rightarrow$
 - (b) $\text{Pb}^{2+}(aq) + \text{CrO}_4^{2-}(aq) \rightarrow$
 - (c) $\text{Hg}_2\text{Cl}_2(s) + \text{NH}_3(aq) \rightarrow$
 - (d) $\text{Ag}(\text{NH}_3)_2^+(aq) + \text{H}^+(aq) + \text{Cl}^-(aq)$.
6. What can you conclude if no precipitate forms when HCl is added to an unknown solution?
7. Why are precipitates washed?
8. How do you decant supernatant liquids from small test tubes?

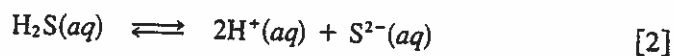
PART B

Chemistry of Group 2 Cations

Hydrogen sulfide is the precipitating agent for the group 2 cations, Pb^{2+} , Cu^{2+} , Bi^{3+} , and Sn^{4+} . We will generate H_2S from the hydrolysis of thioacetamide, CH_3CSNH_2 :



By controlling the hydrogen-ion concentration of the solution, we can control the sulfide-ion concentration. We see from Equation [2], which represents the overall ionization of H_2S , that the equilibrium will shift to the left if the hydrogen-ion concentration is increased by adding some strong acid to the solution.

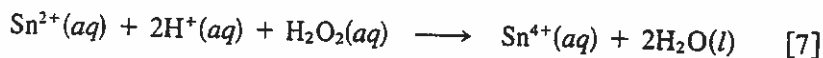


Under these conditions the sulfide-ion concentration is very small. Thus by adjusting the pH of the solution to about 0.5, only the more insoluble sulfides will precipitate. These sulfides are those of group 2, PbS , CuS , Bi_2S_3 , and SnS_2 :

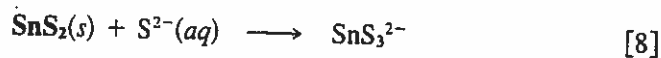


The sulfides of group 3 are soluble in such acidic solutions and therefore do not precipitate because the sulfide ion concentration is too small. The flow chart in Figure 29.3 summarizes how the cations of group 2 are separated and identified. Note the colors of the precipitates. *Consult this scheme often to follow the remaining discussion.*

The cations are first treated with hydrogen peroxide (H_2O_2) and HCl to ensure that tin is in the +4 oxidation state:



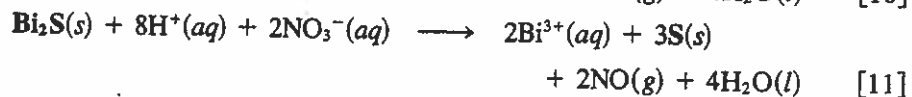
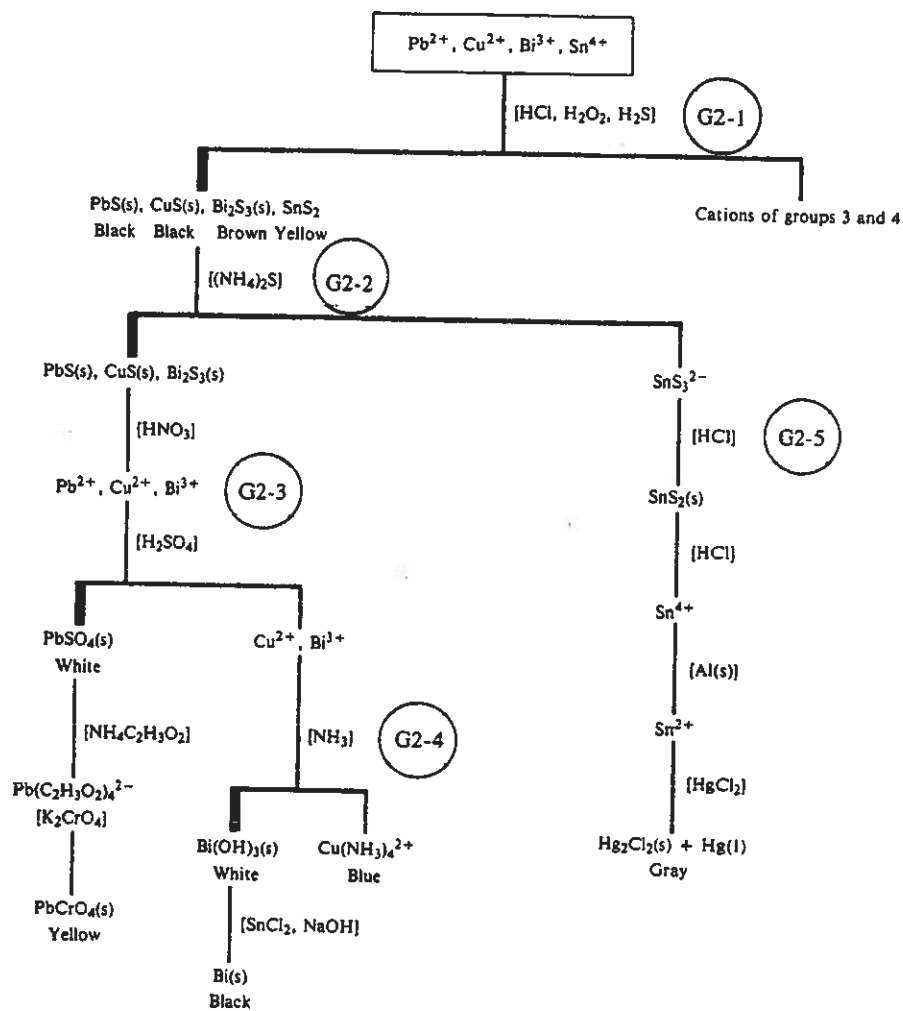
Tin must be in the +4 oxidation state to form the soluble SnS_3^{2-} ion and thereby allow it to be separated from the insoluble sulfides PbS , CuS , and Bi_2S_3 :



These insoluble sulfides are brought into solution by treating them with hot nitric acid. Elemental sulfur is formed in the oxidation reactions:

GROUP 2 CATIONS:
 Pb^{2+} , Cu^{2+} , Bi^{3+} ,
 Sn^{4+}

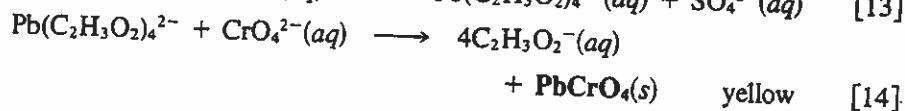
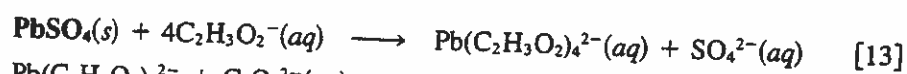
Figure 29.3 Group 2 flow scheme.



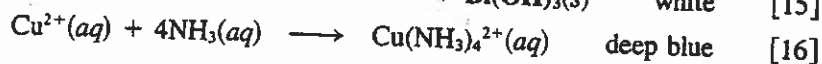
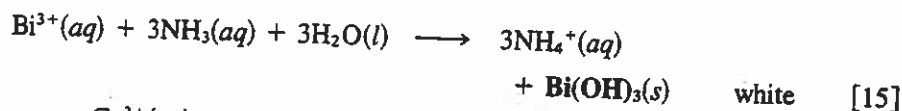
Lead After the sulfides of lead, copper, and bismuth are brought into solution, lead is precipitated as the white sulfate by the addition of H_2SO_4 :



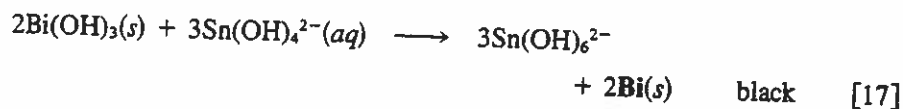
The solution is heated strongly to drive off HNO_3 , because PbSO_4 is soluble in the presence of nitric acid. To confirm the presence of Pb^{2+} , the PbSO_4 is dissolved with $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ and precipitated as yellow PbCrO_4 :



Copper The flow chart of Figure 29.3 shows that addition of aqueous NH_3 to the solution containing Cu^{2+} and Bi^{3+} precipitates Bi^{3+} as white $\text{Bi}(\text{OH})_3$ and forms a soluble deep blue amine complex of copper, $\text{Cu}(\text{NH}_3)_4^{2+}$. The deep blue color confirms the presence of copper and can be seen even when the concentration of copper is very low.



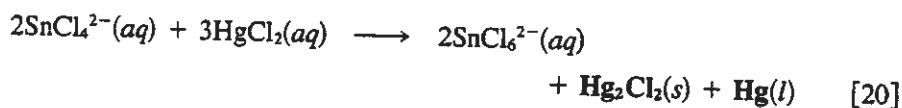
Bismuth The $\text{Bi}(\text{OH})_3$ precipitate is often difficult to observe if the solution is blue. Bismuth is confirmed by separating the $\text{Bi}(\text{OH})_3$ from the solution and reducing it with SnCl_2 in an alkaline solution. A black powder of finely divided bismuth is formed:



Tin Addition of concentrated HCl to a solution of SnS_3^{2-} first yields the precipitate SnS_2 , which eventually dissolves in the acid solution:



Aluminum metal reduces tin from the +4 to the +2 oxidation state. The Sn^{2+} (in the form of the complex SnCl_4^{2-}) in turn reduces HgCl_2 to insoluble Hg_2Cl_2 , which is white, and Hg metal, which is black. Thus the precipitate appears white to gray in color.



G2-1 Oxidation of Sn^{2+} and Precipitation of Group 2

Place the decantate from Procedure G1-1 or 7 drops of "known" or "unknown" solution in a casserole. Add 4 drops of 3% H_2O_2 and 4 drops of 2 M HCl . Carefully boil the solution by passing it back and forth over the flame of your burner. Formation of brown areas on the bottom of the casserole indicates overheating. If brown areas appear, swish the solution around until the brown area disappears. When the volume of the solution is reduced to about 5 drops, stop heating and allow the heat from the casserole to complete the evaporation. About 3 drops of solution should be present after cooling. Add 10 drops of 6 M HCl . IN THE HOOD evaporate the contents of the casserole to a pasty mass, being careful again to avoid overheating. Let the casserole

PROCEDURE

cool, and then add 5 drops of 2 M HCl and 5 drops of distilled water. Swish the contents to dissolve or suspend the residue and transfer it to a small test tube. The solution is evaporated to dryness or to a pasty mass in order to remove the unknown quantity of acid that is present. A known amount of HCl is then added that is required for the group precipitation as sulfides.

Add 10 drops of 1 M thioacetamide to the solution in the test tube. Stir the mixture and heat the test tube in a boiling-water bath for 10 min. (See Appendix J for the use of a hot-water bath.) If excessive frothing occurs, temporarily remove the test tube from the bath. Occasionally stir the solution while it is being heated. After heating for 10 min, add 10 drops of *hot* water and 10 drops of 1 M thioacetamide and 2 drops of 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ (ammonium acetate). Mix and heat in the boiling-water bath for 10 more minutes, stirring occasionally. Cool, centrifuge, and, using a pipet, decant (see Appendix J for the technique) into a test tube. The precipitate contains the group 2 insoluble sulfides, while the supernatant liquid may contain cations from groups 3 and 4.

Test the decantate for completeness of precipitation by adding 3 drops of H_2O , 1 drop of 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, and 2 drops of 1 M thioacetamide. Mix and heat in the boiling-water bath for 1 min. If a colored precipitate forms, continue heating for 3 additional minutes. A faint cloudiness may develop because of the formation of colloidal sulfur. Repeat the precipitation procedure until precipitation is complete. If the decantate is to be analyzed for groups 3 and 4, transfer it to a casserole and boil it to reduce the volume to about 0.5 mL. Otherwise discard it. Transfer the contents to a labeled test tube and save it for Procedure G3-1. Rinse the casserole with 6 drops of water and add the washing to the test tube and stopper it.

All precipitates should be combined into the test tube containing the original precipitate using a few drops of water to aid in the transfer. Wash the precipitate three times, once with 10 drops of *hot* water and twice with 20-drop portions of a hot solution prepared using equal volumes of water and 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. Be certain to stir the washing liquid and precipitate with a stirring rod before each centrifugation. Should the precipitate form a colloidal suspension, add 10 drops of 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ and heat the suspension in the boiling water-bath. Discard the washings. Note, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ is often used in washing of precipitates. Its purpose is to help prevent the precipitate from becoming colloidal. Finely divided particles are difficult to settle.

G2-2 Separation of Sn^{4+} from PbS , CuS , and Bi_2S_3

To the precipitate from Procedure G2-1 add 10 drops of $(\text{NH}_4)_2\text{S}$ (ammonium sulfide) solution and stir well. Then heat for 3 to 4 min in the boiling-water bath. Remove the test tube from the water bath as necessary to avoid excessive frothing. Centrifuge, decant, and save the decantate. Repeat the treatment using 7 drops of $(\text{NH}_4)_2\text{S}$. Centrifuge and combine the decantate with the first. Stopper the combined decantate and save for analysis for tin (Procedure G2-5).

Wash the precipitate twice with 20-drop portions of a hot solution prepared by mixing equal volumes of water and 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. The precipitate may contain PbS , CuS , and Bi_2S_3 and should be analyzed according to Procedure G2-3.

G2-3 Separation and Identification of Pb^{2+}

Add 1 mL (20 drops) of 3 M HNO_3 to the test tube containing the precipitate from Procedure G2-2. Mix thoroughly and transfer the contents to a casserole.

Boil the mixture gently for 1 min. Add more HNO_3 , if necessary, to keep the amount of liquid constant. Cool, centrifuge, and discard any free sulfur that forms. Transfer the decantate to a casserole and add 6 drops of 18 M H_2SO_4 . *Be careful: Concentrated H_2SO_4 causes severe burns.* If you get any on yourself, immediately wash the area with copious amounts of water. In a hood, evaporate the contents until the volume is about 1 drop and dense white fumes of SO_3 are formed. The fumes should be so dense that the bottom of the casserole cannot be seen. The appearance of dense white fumes of SO_3 ensures that all HNO_3 has been removed. Cool, add 20 drops of water, and stir. Quickly transfer the contents to a test tube before the suspended material settles. Cool the test tube. A finely divided white precipitate, PbSO_4 , indicates the presence of lead. Centrifuge and save the decantate for Procedure G2-4. Wash the precipitate twice with 10-drop portions of cold water and discard the washings. Add 6 drops of 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ to the precipitate and stir for about 15 s. Then add 1 drop of 1 M potassium chromate, K_2CrO_4 . The formation of a yellow precipitate (PbCrO_4) confirms the presence of lead.

G2-4 Separation of Bi^{3+} and Identification of Bi^{3+} and Cu^{2+}

To the decantate from Procedure G2-3 carefully add 15 M aqueous NH_3 (avoid inhalation or skin contact) dropwise while constantly stirring until the solution is basic to litmus. The appearance of a deep blue color of $\text{Cu}(\text{NH}_3)_4^{2+}$ confirms the presence of Cu^{2+} . Centrifuge and discard the supernatant liquid, but save the white precipitate of $\text{Bi}(\text{OH})_3$. Be careful in observing the white gelatinous $\text{Bi}(\text{OH})_3$, for it may be somewhat difficult to see when the solution is colored.

Wash the precipitate once with 10 drops of hot water and discard the washings. Add 6 drops of 6 M NaOH and 4 drops of freshly prepared* 0.2 M SnCl_2 to the precipitate and stir. The formation of a jet-black precipitate confirms the presence of Bi^{3+} .

G2-5 Identification of Sn^{4+}

Transfer the decantate from procedure G2-2 to a casserole and boil for 1 min to expel H_2S ; then add 4 drops of cold water. Add a 1-in. piece of 26 gauge aluminum wire and heat gently until the wire has dissolved. Continue to gently heat the solution for about 2 more minutes, replenishing the solution with 6 M HCl if necessary. There should be no dark residue at this stage; if there is, continue heating until it dissolves. (You cannot stop at this point.) Transfer the solution to a test tube and cool under running water. Immediately add 3 drops of 0.1 M mercuric chloride, HgCl_2 , and mix. Allow the mixture to stand for 1 min. The formation of a white or gray precipitate confirms the presence of tin.

REVIEW QUESTIONS

Before beginning Part B of this experiment in the laboratory, you should be able to answer the following questions:

*Solid tin should be present in the bottle to ensure that tin is in the +2 oxidation state.

1. Give the symbols and charges of the cations of group 2.
2. How could CuS be separated from SnS₂?
3. How are Cu²⁺ and Bi³⁺ separated?
4. How can Ag⁺ be separated from Cu²⁺?
5. Complete and balance the following equations:
 - (a) Bi³⁺(aq) + S²⁻(aq) →
 - (b) SnS₂(s) + S²⁻(aq) →
 - (c) PbS(s) + H⁺(aq) + NO₃⁻(aq) →
 - (d) Bi³⁺(aq) + NH₃(aq) + H₂O(l) →
6. Why is H₂O₂ added in the initial step of the separation of group 2 cations?
7. What is the color of CuS? Of SnS₂? Of PbSO₄?

PART C

GROUP 3 CATIONS: Fe³⁺, Ni²⁺, Mn²⁺, Al³⁺

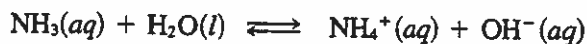
Chemistry of Group 3 Cations

The group 3 cations that we will consider are Fe³⁺, Ni²⁺, Mn²⁺, and Al³⁺. These cations do not precipitate as insoluble chlorides (as do those of group 1) or as sulfides in acidic solution (like those of group 2). These ions can be separated from those of group 4 by precipitation as insoluble hydroxides or sulfides under slightly alkaline conditions. The separation is shown in the flow chart of Figure 29.4. As in group 2, the pH of the solution controls the sulfide-ion concentration. The slightly alkaline conditions employed here favor a higher sulfide-ion concentration than that used in the group 2 separation. FeS, NiS, and MnS are more soluble than the sulfides of group 2 and therefore require a higher sulfide-ion concentration for their precipitation. Making the solution slightly alkaline reduces the hydrogen ion concentration. We see that decreasing the hydrogen ion concentration causes the following equilibrium to shift to the right:



This results in an increase in the sulfide ion concentration.

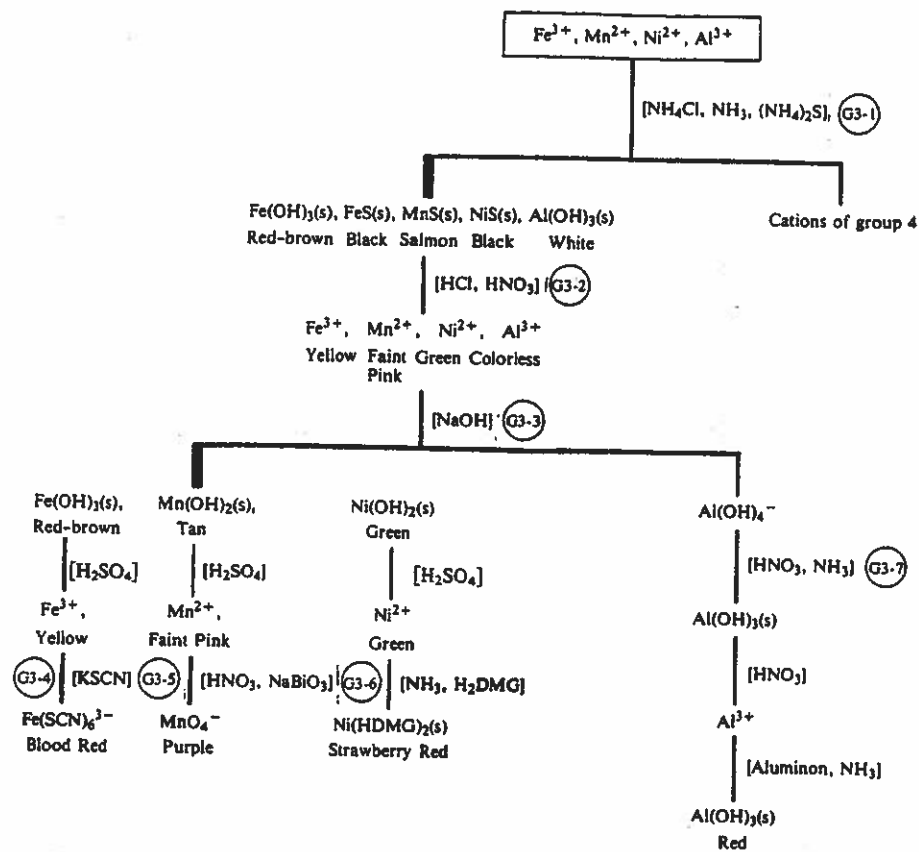
Aqueous ammonia is a weak base:



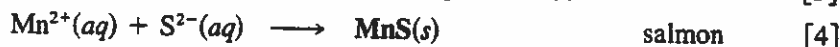
A mixture of aqueous NH₃ and NH₄Cl makes a buffer solution whose pH allows the precipitation FeS, MnS, and NiS. Moreover, in this slightly alkaline solution, the insoluble hydroxides of Fe(OH)₃ and Al(OH)₃ also precipitate. Although Mg(OH)₂ is insoluble, it does not precipitate with the group 3 hydroxides because the OH⁻ ion concentration is too small. The common ion NH₄⁺, from NH₄Cl controls the OH⁻ concentration and keeps it sufficiently low, preventing the Mg(OH)₂ from precipitating.

As you analyze the group 3 ions, pay particular attention to the colors of the solutions and the precipitates. Aqueous solutions of Al³⁺ ions are colorless, while those of Fe³⁺ appear yellow to reddish-brown; Ni²⁺ solutions are green, and Mn²⁺, very faint pink.

Figure 29.4 Group 3 flow scheme.



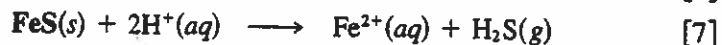
The reactions involved in the precipitation of the group 3 cations are:

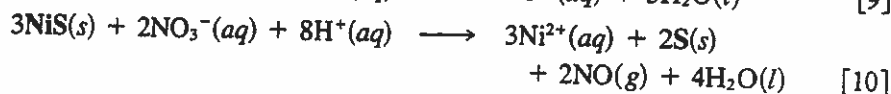


In aqueous NH_3 solution, Ni^{2+} ions exist as the ammine complex $\text{Ni}(\text{NH}_3)_6^{2+}$, and addition of $(\text{NH}_4)_2\text{S}$ results in the precipitation of NiS . Some $\text{Fe}(\text{OH})_3$ is reduced by sulfide:

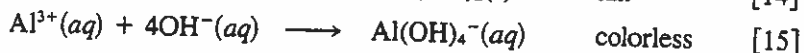
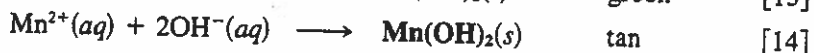


The group 3 precipitates are dissolved using HCl . Nitric acid is also added to help dissolve NiS by oxidizing S^{2-} ions to elemental sulfur. At the same time, nitric acid oxidizes Fe^{2+} to Fe^{3+} :



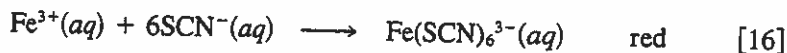


After all ions are in solution, addition of excess strong base allows the separation of Fe^{3+} , Ni^{2+} , and Mn^{2+} ions from Al^{3+} ions. Fe(OH)_3 , Ni(OH)_2 , and Mn(OH)_2 precipitate, while Al(OH)_3 , being amphoteric, redissolves in excess base forming aluminate ions:

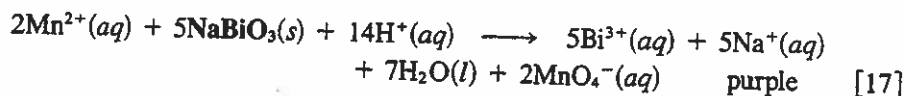


The hydroxide precipitates are dissolved by the addition of H_2SO_4 to give a solution of Fe^{3+} , Ni^{3+} , and Mn^{2+} ions. After the solution is divided into three equal parts, tests for the individual ions are made as described below.

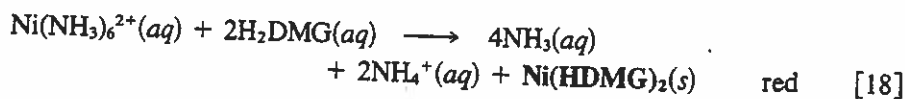
Iron A very sensitive test for Fe^{3+} uses the thiocyanate ion, SCN^- . If Fe^{3+} is present, a blood-red solution results when SCN^- is added:



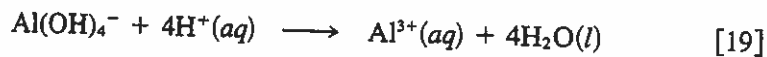
Manganese Because of its intense purple color, the permanganate ion, MnO_4^- , affords a suitable confirmatory test for Mn^{2+} . When a solution of Mn^{2+} is acidified with HNO_3 and then treated with sodium bismuthate, NaBiO_3 , Mn^{2+} is oxidized to MnO_4^- :



Nickel The presence of Ni^{2+} is confirmed by the formation of a bright red precipitate when an organic compound called dimethylglyoxime (abbreviated as H_2DMG) is added to an ammoniacal solution:



Aluminum When a solution that contains Al(OH)_4^- is acidified and then made slightly alkaline with the weak base NH_3 , Al(OH)_3 precipitates:



Aluminum hydroxide is not easily seen, for it is a gelatinous, translucent substance. To help see the hydroxide it is precipitated in the presence of a red dye. The dye is absorbed on the Al(OH)_3 , giving it a cherry-red color.

G3-1 Precipitation of Group 3 Cations

Place the decantate from Procedure G2-1 or 7 drops of known or unknown solution in a small (10 mm × 75 mm) test tube. If the decantate from Procedure G2-1 has a precipitate, centrifuge, decant, and discard the precipitate. Add 5 drops of 2 M NH_4Cl and stir; add 15 M NH_3 dropwise with stirring, until the solution is just basic. Usually this requires only a few drops of the NH_3 . Then add 2 additional drops of the 15 M NH_3 and 1 mL (20 drops) of water. Stir thoroughly. Next add 10 drops of $(\text{NH}_4)_2\text{S}$ and mix thoroughly. Heat the test tube in a boiling-water bath for about 5 min. If excessive frothing occurs, temporarily remove the test tube from the hot-water bath. Centrifuge and test for completeness of precipitation using 1 drop of $(\text{NH}_4)_2\text{S}$. Note the color of the precipitate. Decant and save the decantate for group 4 analysis, or discard, as appropriate.

Wash the precipitate two times with 20 drops of a solution made by mixing equal portions of water and 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. For each washing, stir the precipitate with the wash solution and heat the mixture in the water bath before centrifuging. Discard the supernatant wash liquid.

G3-2 Dissolution of Group 3 Precipitate

Treat the precipitate from Procedure G3-1 with 12 drops of 12 M HCl , and cautiously add 5 drops of 16 M HNO_3 and carefully mix the solution (CAUTION: HNO_3 can cause severe burns. If you come in contact with the acid, wash the area with copious amounts of water). Heat the test tube in the hot-water bath until the precipitate dissolves and a clear, but not necessarily colorless, solution is obtained. Add 10 drops of water, centrifuge to remove any sulfur that has precipitated, and decant into a casserole. Note the color of the decantate.

G3-3 Separation of Iron, Nickel, and Manganese from Aluminum

Make the solution in the casserole from Procedure G3-2 strongly basic, using 6 M NaOH , mixing thoroughly. If the precipitate is pasty and nonfluid, add 12 drops of water. Note the color of the precipitate. Transfer to a test tube and centrifuge. Decant, saving the decantate, which may contain aluminum, for Procedure G3-7. To the precipitate add 20 drops of water and 10 drops of 6 M H_2SO_4 . Stir and heat in a water bath for 3 min or until the precipitate dissolves. Add 12 drops of water and divide the solution into three approximately equal volumes.

G3-4 Test for Fe^{3+}

To one of the three samples from Procedure G3-3 add 2 drops of 0.2 M KSCN (potassium thiocyanate). A blood-red solution confirms the presence of iron as $\text{Fe}(\text{SCN})_6^{3-}$. Traces of iron that have been introduced as impurities along the way will give a weak test. If you are in doubt about your results, perform this test on 10 drops of your original sample.

G3-5 Test for Mn^{2+}

To the second portion of a solution from Procedure G3-3 add an equal volume of water and 4 drops of 3 M HNO_3 . Mix, and then add a few grains of solid sodium bismuthate, NaBiO_3 . Mix thoroughly with a stirring rod and cen-

trifuge. A pink or purple color is due to MnO_4^- and confirms the presence of manganese.

G3-6 Test for Ni^{2+}

To a third portion of the sample from Procedure G3-3 add 6 M NH_3 until the solution is basic. If a precipitate forms, remove it by centrifuging and decanting, keeping the decantate. Add about 4 drops of dimethylglyoxime reagent mix, and allow to stand. The formation of a strawberry-red precipitate indicates the presence of nickel.

G3-7 Test for Al^{3+}

Treat only half of the decantate from Procedure G3-3 with 16 M HNO_3 until the solution is slightly acidic. (CAUTION: HNO_3 can cause severe burns. Wash with water immediately if you come in contact with the acid.) Then add 15 M NH_3 while stirring until the solution is distinctly alkaline. Allow at least 1 min for the formation of $\text{Al}(\text{OH})_3$. Centrifuge and carefully remove the supernatant liquid with a capillary pipet without disturbing the gelatinous $\text{Al}(\text{OH})_3$. Discard the supernate. Wash the precipitate two times with 20 drops of hot water, discarding the decantate. Dissolve the precipitate in 7 drops of 3 M HNO_3 . Add 3 drops of aluminon reagent, which colors the solution; stir; and add 6 M NH_3 dropwise until the solution is just alkaline (avoid an excess). Stir and centrifuge. The formation of a cherry-red precipitate, not solution, confirms the presence of aluminum.

REVIEW QUESTIONS

Before beginning Part C of this experiment in the laboratory, you should be able to answer the following questions:

1. What are the symbols and charges of the group 3 cations?
2. What are the colors of the following ions: Cu^{2+} , Fe^{3+} , Al^{3+} , Ni^{2+} ?
3. What are the colors of the following solids: $\text{Fe}(\text{OH})_3$, MnS , $\text{Al}(\text{OH})_3$, $\text{Ni}(\text{OH})_2$?
4. How can Fe^{3+} be separated from Al^{3+} ?
5. How can $\text{Ni}(\text{OH})_2$ be separated from $\text{Al}(\text{OH})_3$?
6. Complete and balance the following equations:
 - (a) $\text{Fe}^{3+}(\text{aq}) + \text{OH}^{-}(\text{aq}) \longrightarrow$
 - (b) $\text{Al}(\text{OH})_3(\text{s}) + \text{H}^{+}(\text{aq}) \longrightarrow$
 - (c) $\text{FeS}(\text{s}) + \text{H}^{+}(\text{aq}) \longrightarrow$
 - (d) $\text{NiS}(\text{s}) + \text{NO}_3^{-}(\text{aq}) + \text{H}^{+}(\text{aq}) \longrightarrow$
7. Give the formula for a reagent that precipitates
 - (a) Pb^{2+} but not Ni^{2+}
 - (b) Fe^{3+} but not Al^{3+}
8. What cation forms a
 - (a) Blood-red solution with thiocyanate ion?
 - (b) Bright red precipitate with dimethylglyoxime?
9. If solid NH_4Cl is added to 3 M NH_3 , does the pH increase, decrease or remain the same?

Chemistry of Group 4 Cations

In addition to the ammonium ion, the cations of group 4 consist of ions of the alkali and alkaline earth metals. The cations we will consider in this group are Ba^{2+} , Ca^{2+} , NH_4^+ , and Na^+ . Because their chlorides and sulfides are soluble, these ions do not precipitate with groups 1, 2, or 3.

Sodium ions are a common impurity and were even introduced (as was ammonium ion) in some of the reagents that were used in the analysis of groups 1, 2, and 3. Hence, in the analysis of a general unknown mixture, tests for these ions must be made on the original sample even before performing the group analysis. The flow scheme for group 4 is shown in Figure 29.5.

Barium Because barium chromate, BaCrO_4 ($K_{sp} = 1.2 \times 10^{-10}$), is more insoluble than calcium chromate, CaCrO_4 ($K_{sp} = 7.1 \times 10^{-4}$), Ba^{2+} can be separated from Ca^{2+} by precipitation as the insoluble yellow chromate salt:



BaCrO_4 is insoluble in the weak acid $\text{HC}_2\text{H}_3\text{O}_2$, but it is soluble in the presence of the strong acid HCl , because it is the salt of a weak acid. After BaCrO_4 is dissolved in HCl , a flame test is performed on the resulting solution. A green-yellow flame is indicative of Ba^{2+} . Further confirmation of Ba^{2+} is precipitation of BaSO_4 , which is white:



Calcium Calcium oxalate, CaC_2O_4 , is very insoluble ($K_{sp} = 4.0 \times 10^{-9}$). The formation of a white precipitate when oxalate ion is added to a slightly alkaline solution confirms the presence of Ca^{2+} :

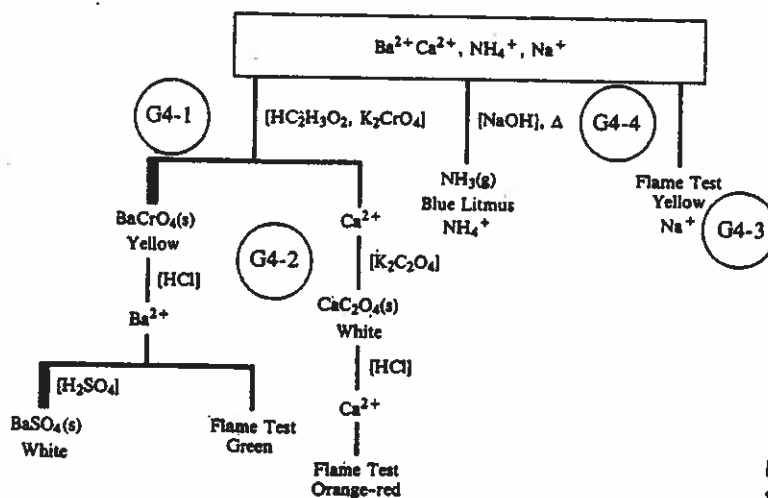


Figure 29.5 Group 4 flow scheme.

Additional evidence for the calcium ion is obtained from a flame test. Dissolution of CaC_2O_4 with HCl , followed by a flame test, produces an orange-red flame that is characteristic of calcium ions.

Sodium Most sodium salts are soluble. The simplest test for sodium ion is a flame test. Sodium salts impart a characteristic yellow color to a flame; the test is very sensitive, and because of the prevalence of sodium ions, much care must be exercised to keep equipment clean and free from contamination by these ions.

Ammonium The ammonium ion, NH_4^+ , is the conjugate acid of the base ammonia, NH_3 . The test for NH_4^+ takes advantage of the following equilibrium:



Thus, when a strong base is added to a solution of an ammonium salt and this solution is heated, NH_3 gas is evolved. The NH_3 can easily be detected by its effect upon red litmus.

PROCEDURE

G4-1 Separation and Identification of Ba^{2+}

If the solution, "known," or "unknown" contains only cations of group 4, place 7 drops of the solution in a small test tube; otherwise, use the supernate from group 3 analysis, Procedure G3-1. Add 8 drops of 6 *M* acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, and 1 drop of 1 *M* K_2CrO_4 and mix. The formation of a yellow precipitate indicates the presence of Ba^{2+} . Centrifuge, saving the decantate for Procedure G4-2 to test for calcium. Dissolve the precipitate with 6 *M* HCl and perform a flame test as described below.

To perform the flame test, obtain a piece of platinum or Nichrome wire that has been sealed in a piece of glass tubing. Clean the wire by dipping it in 12 *M* HCl that is contained in a small test tube and heat the wire in the hottest part of your Bunsen burner flame. Repeat this operation until no color is seen when the wire is placed in the flame. Several cleanings will be required before this is achieved. Then dip the wire into the solution to be tested and place the wire in the flame. A pale green flame confirms the presence of Ba^{2+} . If the concentration of Ba^{2+} is very low, you may not detect the green color.

As further confirmation of barium, add 10 drops of 6 *M* H_2SO_4 to the solution on which the flame test was performed. A white precipitate confirms the presence of Ba^{2+} .

G4-2 Test for Ca^{2+}

Make the decantate from Procedure G4-1 alkaline to litmus with 15 *M* NH_3 . If a precipitate forms, centrifuge and discard the precipitate. Add 7 drops of 1 *M* $\text{K}_2\text{C}_2\text{O}_4$ (potassium oxalate) and stir. The formation of a white precipitate indicates the presence of calcium ion. Should no precipitate form immediately, warm the test tube briefly in the hot-water bath and then cool.

Additional evidence for Ca^{2+} is obtained from a flame test. Dissolve the precipitate in 6 *M* HCl and then perform a flame test. A transitory red-orange

color that appears when the wire is first placed in the flame and later reappears somewhat more red as the wire is heated is characteristic of the calcium ion. If the concentration of Ca^{2+} is very low, you may not observe the red color.

G4-3 Test for Na^+

The flame test for sodium is sensitive, and traces of sodium ion will impart a characteristic yellow color to the flame. Just about every solution has a trace of sodium and thus will give a positive test. On the basis of the intensity and duration of the yellow color, you can decide whether Na^+ is merely a contaminant or present in substantial quantity. Using a clean wire, perform a flame test on your original (untreated) unknown. To help you make a decision as to the presence of sodium, run a flame test on distilled water and then on a 0.2 M NaCl solution. Compare the tests.

G4-4 Test for NH_4^+

Place 2 mL of the original (untreated) unknown or known in a 100-mL beaker (or casserole) and add 2 mL of 6 M NaOH. Moisten a piece of red litmus paper with water and stick it to the convex side of a small watch glass. Cover the beaker with the watch glass convex side down. (The litmus paper must not come into contact with any NaOH.) Gently warm the beaker with a small burner flame; do not boil. Allow the covered beaker to stand 3 min. A change in the color of the litmus paper from red to blue confirms the presence of ammonium ion.

REVIEW QUESTIONS

Before beginning Part D of this experiment in the laboratory, you should be able to answer the following questions:

1. What are the symbols and charges of the group 4 cations?
2. Which is less soluble: BaCrO_4 or CaCrO_4 ?
3. What is the color of
 - (a) BaSO_4 ?
 - (b) BaCrO_4 ?
 - (c) CaC_2O_4 ?
4. What color do the following ions impart to a flame:
 - (a) Ba^{2+} ?
 - (b) Ca^{2+} ?
 - (c) Na^+
5. What reagent will precipitate
 - (a) Cu^{2+} but not Ba^{2+} ?
 - (b) Ag^+ but not Ca^{2+} ?
 - (c) Ba^{2+} but not NH_4^+ ?
6. Complete and balance the following equations:
 - (a) $\text{Ba}^{2+}(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$
 - (b) $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$