

QUALITATIVE ANALYSIS OF THE GROUP I CATIONS: Ag^+ , Pb^{2+} , Hg_2^{2+}

SEPARATION OF THE GROUP I CATIONS

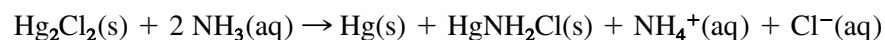
In the classical qualitative analysis scheme, the first ions which are determined are Ag^+ , Pb^{2+} , and Hg_2^{2+} . Of all the common cations, only these form insoluble chlorides under acidic conditions. These cations comprise Group I in the scheme and are separated from a general salt solution by precipitation of their chlorides at a pH of about zero. The chloride precipitate is then analyzed for the possible presence of silver, lead, and mercury(I) on the basis of the characteristic properties of those cations.

PROPERTIES OF THE GROUP I CATIONS

Ag^+ . Silver has only a few water-soluble salts, of which nitrate is certainly the most common. Most of the insoluble silver salts dissolve in cold 6 M HNO_3 , the main exceptions being the silver halides, AgSCN , and Ag_2S . Silver ion forms many stable complexes; of these, the best known is probably the $\text{Ag}(\text{NH}_3)_2^+$ ion. This complex is sufficiently stable to be produced when AgCl or AgSCN is treated with 6 M NH_3 ; the reaction which occurs is useful for dissolving those solids. AgBr and AgI are less soluble than AgCl ; AgBr will go into solution in 15 M NH_3 , but AgI is so insoluble that it will not. The silver thiosulfate complex ion, $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$, is extremely stable, and is important in photography, where it is formed in the “fixing” reaction in which AgBr is removed from the developed negative.

Pb^{2+} . Lead nitrate and acetate are the only well-known soluble lead salts. Lead chloride is not nearly as insoluble in water as are the chlorides of silver and mercury(I), and becomes moderately soluble if the water is heated. PbSO_4 is one of the relatively few insoluble sulfates. Lead forms a stable hydroxide complex ion and a weak chloride complex. Although lead ordinarily has an oxidation number of +2, there are some Pb(IV) compounds, of which the most common is PbO_2 (brown); this compound is insoluble in most reagents, but will dissolve in 6 M HNO_3 to which some H_2O_2 has been added.

Hg_2^{2+} . Mercury(I) has only one soluble salt, the nitrate, and even with this compound, excess HNO_3 must be present to keep basic Hg(I) salts from precipitating. The Hg(I) ion, sometimes called mercurous ion, is relatively unstable; it will slowly oxidize to Hg(II) if exposed to air, and can be reduced to the metal by reducing cations (e.g., Sn^{2+}). In the presence of species that form Hg(II) complex ions or insoluble salts, mercurous ion often undergoes a disproportionation reaction to Hg (solid, black) and the Hg(II) compound. Mercury(I) chloride has a very characteristic reaction with ammonia:



In Table 31.1 we have summarized some of the general solubility properties of the Group I cations. There is a good deal of information in the table, and you should learn to properly interpret and use the information it contains. For example, in the entry for Ag^+ and CrO_4^{2-} we

Table 1 Solubility Properties of the Group I Cations

| | Ag^+ | Pb^{2+} | Hg_2^{2+} |
|---|---|-------------------------------|----------------------------|
| Cl^- | C, A ⁺ (white) | HW, C, A ⁺ (white) | O ⁺ (white) |
| OH^- | C, A (brown) | C, A (white) | D (black) |
| SO_4^{2-} | S ⁻ , C (white) | C (white) | S ⁻ , A (white) |
| CrO_4^{2-} | C, A (dk red) | C (yellow) | A (orange) |
| CO_3^{2-} , PO_4^{3-} | C, A (white) | C, A (white) | A (white) |
| S^{2-} | O (black) | O (black) | D (black) |
| Complexes | NH_3 , $\text{S}_2\text{O}_3^{2-}$ | OH^- | — |

Key: *S*, soluble in water, > 0.1 mole/liter. *S*⁻, slightly soluble in water, ~ 0.01 mole/liter. *HW*, soluble in hot water. *A*, soluble in acid (6 M HCl or other nonprecipitating, nonoxidizing acid). *I*, insoluble in any common solvent.

A⁺, soluble in 12 M HCl. *B*, soluble in hot 6 M NaOH containing S^{2-} ion. *O*, soluble in hot 6 M HNO_3 . *O*⁺, soluble in hot aqua regia. *C*, soluble in solution containing a good complexing ligand. *D*, unstable, decomposes.

have C, A (dk red). This means that if water solutions containing Ag^+ and CrO_4^{2-} ions are mixed, we obtain a precipitate of dark red Ag_2CrO_4 ; this substance is not soluble in water but would dissolve in an acidic solution such as 6 M HNO_3 (A), which would not contain a precipitating anion, and in solutions containing ligands which form stable complexes with silver (C). The entry opposite Complexes tells us that those ligands normally encountered in qualitative analysis include NH_3 and $\text{S}_2\text{O}_3^{2-}$.

GENERAL SCHEME OF ANALYSIS

The procedure used for the qualitative analysis of the Group I cations makes simple, straightforward use of some of the properties of these ions. Following separation of the chloride precipitate, the solid is treated with hot water to dissolve any PbCl_2 that is present. The hot solution containing Pb^{2+} ion is then mixed with a solution of K_2CrO_4 ; if lead is present, a yellow precipitate of PbCrO_4 will be produced. The remaining chloride precipitate is treated with 6 M NH_3 . If Hg(I) is present, a black precipitate containing Hg(s) will form. Any silver chloride present will dissolve as $\text{Ag}(\text{NH}_3)_2^+$; after separation from the solid, the solution of the silver complex ion is acidified, which destroys the complex and reprecipitates white AgCl . In the presence of large amounts of Hg_2^{2+} , silver ion may be reduced to metallic silver on addition of NH_3 to the chloride precipitate; under such conditions the black precipitate which is obtained in that step is dissolved in aqua regia, and the resulting solution is tested for silver.

**WEAR YOUR SAFETY GLASSES WHILE
PERFORMING THIS EXPERIMENT
DISCARD ALL REACTION PRODUCTS
IN WASTE CROCK**



Procedure for Analysis of Group I Cations

Unless told otherwise, you may assume that 10 mL of your sample contains the equivalent of about 1 mL of 0.1 M solutions of the nitrate salts of one or more of the Group I cations, plus possibly ions from group II, III, and IV. Roughly speaking, this amounts to about 10 mg of each cation present. This is a sufficient amount for good qualitative tests, *as long as you do not lose any component cations* by improperly carrying out or interpreting any step.

Step 1. To 3 mL of your sample in a test tube, add 0.5 mL 6 M HCl. Stir well and centrifuge. Decant the liquid, which may contain ions from groups to be discussed later, into a test tube and save it, if necessary, for further analysis; to make sure precipitation of Group I cations was complete, add one drop of 6 M HCl to the liquid. Wash the

precipitate with 2 mL water and three drops of 6 M HCl. Stir well. Centrifuge and discard the wash liquid. Wash the precipitate again with water and HCl; centrifuge and discard the wash.

- Step 2.** To the precipitate from Step 1, which contains the chlorides of the Group I cations, add about 4 mL water. Heat in the boiling water bath for at least 3 minutes, stirring constantly. Centrifuge quickly and decant the liquid, which may contain Pb^{2+} , into a test tube.
- Step 3. Confirmation of the Presence of Lead.** To the liquid from Step 2, add two drops of 6 M acetic acid and three or four drops of 0.5 M K_2CrO_4 . The formation of a yellow precipitate of PbCrO_4 confirms the presence of lead. Centrifuging out the solid may help with the identification, because the liquid phase is orange.
- Step 4. Confirmation of the Presence of Mercury.** If lead is present, wash the precipitate from Step 2 with 6 mL water in the boiling water bath. Centrifuge and test the liquid for Pb^{2+} . Continue the washings until no positive reaction to the lead test is obtained. To the washed precipitate add 2 mL 6 M NH_3 and stir well. A black or dark gray precipitate establishes the presence of the mercury(I) ion. Centrifuge and decant the liquid, which may contain $\text{Ag}(\text{NH}_3)_2^+$, into a test tube.
- Step 5. Confirmation of the Presence of Silver.** To the liquid from Step 4 add 3 mL 6 M HNO_3 . Check with litmus to see that the solution is acidic. A white precipitate of AgCl confirms the presence of silver.
- Step 6. Alternative Confirmation of the Presence of Silver.** If the test for silver ion was inconclusive, and mercury was present, go back to the precipitate from Step 4. Wash the precipitate with 3 mL of water, centrifuge, and discard the liquid. To the precipitate add 1 mL 6 M HCl and 1 mL 6 M HNO_3 , and put the test tube in the water bath. Within a minute or two all of the mercury-containing species will dissolve, leaving, if silver is present, a curdy, bluish-gray precipitate of AgCl . Centrifuge out the precipitate, and carefully decant the liquid, making sure not to decant the solid. Wash the solid with 2 mL water, centrifuge, and discard the wash. To the solid add 1 mL 6 M NH_3 ; with stirring, the precipitate should dissolve. Then add 6 M HNO_3 until the solution is acidic. If silver is present, a white precipitate of AgCl will form.

Comments on Procedure for Analysis of Group I Cations

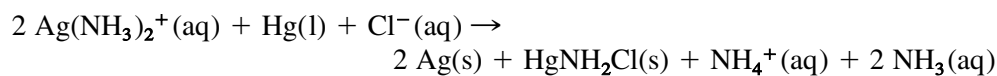
- Step 1.** In this step the cations of Group I are precipitated as their chlorides. Both silver and lead ions can form chloride complexes in solutions when the chloride ion concentrations are high. In our procedure, $[\text{Cl}^-]$ is about 1 M, which decreases the salt solubilities by the common ion effect but is not great enough to cause appreciable amounts of the complex ions to form. If, of the Group I cations, only lead is present, it may not precipitate unless its concentration is ~ 0.1 M or greater.
- Step 2.** The PbCl_2 is sufficiently soluble in hot water to allow its separation from the other chlorides by simply heating the precipitate, with mixing, in water. The centrifuging should be done quickly to avoid reprecipitation of PbCl_2 on cooling.
- Step 3.** We acidify the liquid to minimize precipitation of other chromates from residual amounts of ions in other groups. The liquid is orange because of the conversion of CrO_4^{2-} to $\text{Cr}_2\text{O}_7^{2-}$ in the acid medium.
- Step 4.** If lead chloride is not completely removed, it is converted to a white, basic, insoluble salt on addition of NH_3 . This could cause confusion, but should not interfere with later identifications. The AgCl dissolves readily in 6 M NH_3 , with formation of

EXPERIMENT **Qualitative Analysis of the Group I Cations: Ag⁺, Pb²⁺, Hg₂²⁺**

the silver ammonia complex ion. If Hg₂Cl₂ is present, it reacts with NH₃, forming black Hg and white insoluble HgNH₂Cl. The mixture is black or dark gray if mercury(I) ion is present.

Step 5. The silver ammonia complex ion is destroyed by acid, and the released silver ion precipitates with the chloride ion in solution. The formation of white AgCl is definitive evidence for the presence of silver.

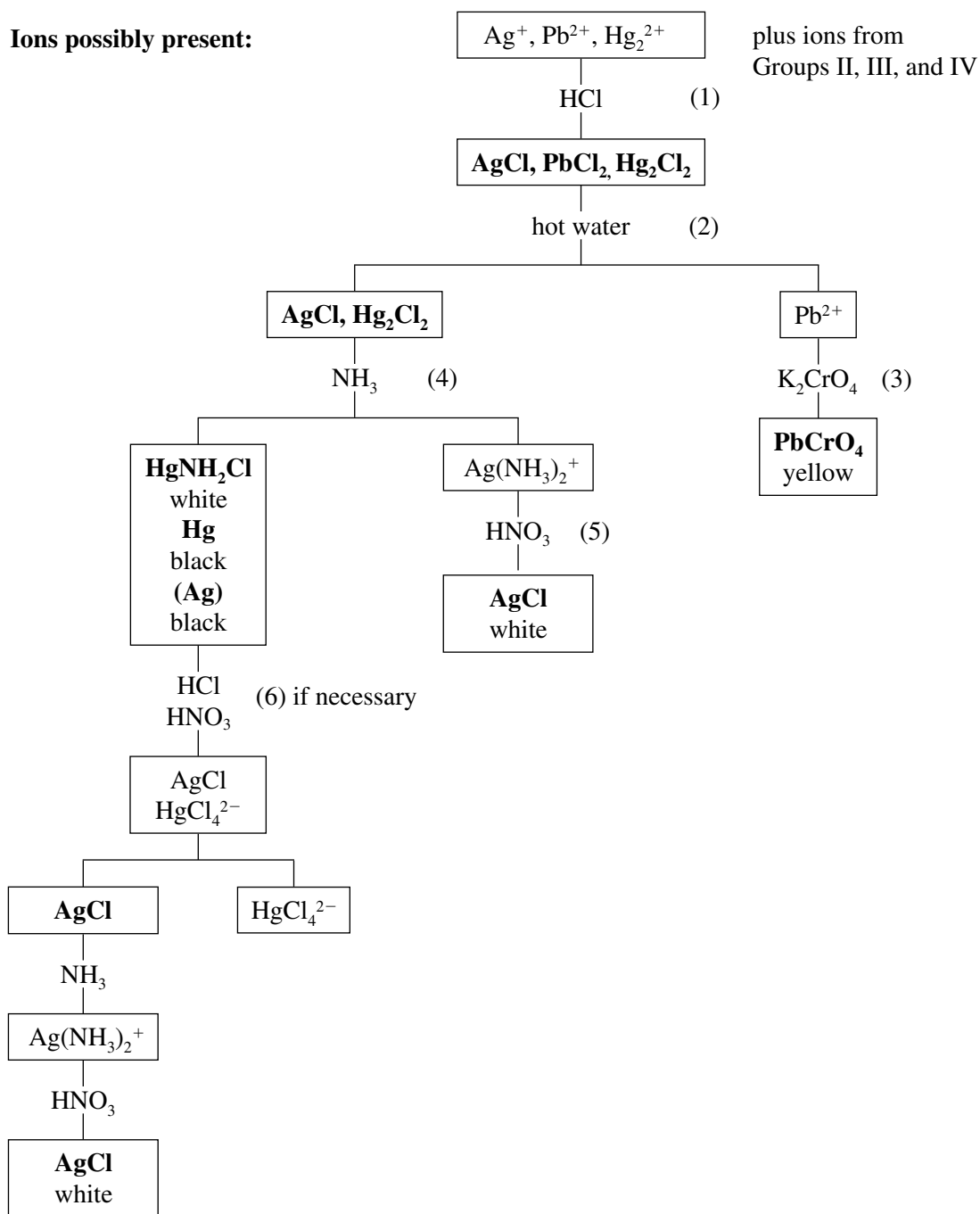
Step 6. If both mercury(I) ion and silver ion are present, the Ag(NH₃)₂⁺ and mercury, both present in Step 4, tend to undergo an oxidation-reduction reaction:



If sufficient mercury is present, nearly all of the silver will be reduced and a very doubtful test for Ag⁺ obtained in Step 5. If it appears that this may be the case, carrying out Step 6 should be helpful. On being dissolved in aqua regia, the mercury exists as HgCl₄²⁻ or HgCl₂; the silver is converted to AgCl. The solution of AgCl in NH₃ and reprecipitation on addition of HNO₃ is definitive confirmation of the presence of silver.

Outline of Procedure for Analysis of Group I Cations (Group I Flow Chart)

Ions possibly present:



LABORATORY ASSIGNMENTS

Perform one or more of the following, as directed by your instructor:

1. Make up a sample containing about 1 mL of 0.1 M solutions of the nitrate salts of each of the cations in Group I. Go through the standard procedure for analysis of the Group I cations, comparing your observations with those that are given. Then obtain a Group I unknown from your instructor and analyze it to determine possible presence of Ag^+ , Pb^{2+} , and Hg_2^{2+} . On a Group I flow chart, indicate your observations and conclusions about the unknown, and submit the completed chart to your instructor.
2. If a sample may contain *only* cations from Group I, it is possible to analyze it by several procedures that are quite different from the one given in this book. Develop a scheme for analysis of such a sample, starting with the addition of 6 M NaOH in excess. Draw a complete flow chart for your procedure, indicating reagents to be added at each step and the formulas and colors of all species present during the course of the analysis. Test your procedure with a Group I known, and then use your method to analyze an unknown sample. In another color, indicate on your flow chart your observations on the unknown and your conclusions regarding its composition.

Note: In this and all succeeding laboratory assignments in this manual, the first assigned problem involves your acquiring some familiarity with the standard procedure for analysis. Succeeding problems require your developing and using your own schemes for analyzing particular unknown mixtures. In setting up your procedures, you may use steps from the standard schemes, but you should also examine the characteristic properties of the individual ions to see if some of them might be profitably used in your scheme. In all probability, the best method for analyzing any given limited mixture of ions will be partly based on the standard procedure and partly based on ion properties that were not made use of in the standard approach.

Experiment

Name _____

Section _____

Observations: Analysis of Group I Cations

Assignment 1: Flow Chart Showing Behavior of Unknown

Cations present

Unknown no. _____

Assignment 2: Flow Chart

Advance Study Assignment: Analysis of Group I Cations

1. Write balanced net ionic equations for the following reactions:
 - a. The precipitation of the chloride of Hg_2^{2+} .
 - b. The dissolving of PbCl_2 in hot water.
 - c. The dissolving of AgCl in aqueous ammonia.
2. You are given an unknown solution that contains only one of the Group I cations and no other metallic cations. Develop the simplest procedure you can think of to determine which cation is present. Draw a flow chart showing the procedure and the observations to be expected at each step with each of the possible cations.
3. A solution may contain Ag^+ , Pb^{2+} , and Hg_2^{2+} . A white precipitate forms on addition of 6 M HCl. The precipitate is insoluble in hot water. The residue turns black on addition of ammonia. Which of the ions are present, which are absent, and which remain undetermined? State your reasoning. *Note:* On paper unknowns such as this one, confirmatory tests are usually not included.

Present _____

Absent _____

In doubt _____

