



Qualitative Analysis of Group I Cations: Precipitation and Separation of Group I Ions

PURPOSE

To provide an overview of a general scheme for separating and identifying **ten** cations. To introduce the laboratory techniques used in qualitative analysis. To begin the study of the first group of three cations, Ag^+ , Pb^{2+} , and Hg_2^{2+} ions, which are separated out as insoluble chloride salts.

PRE-LAB PREPARATION

Qualitative analysis is a branch of analytical chemistry that identifies particular substances in a given sample of material. In the analysis of inorganic substances, this branch involves the analysis of both metallic constituents as cations and nonmetallic constituents as anions. This and the next four experiments constitute a series in qualitative analysis. The next three experiments (Qualitative group I, III, IV, and V) deal with the identification of ten common cations, including Ag^+ , Pb^{2+} , Hg_2^{2+} , Fe^{3+} , Al^{3+} , Zn^{2+} , Ca^{2+} , Ba^{2+} , K^+ , and NH_4^+ . The fourth experiment, explores the identification of seven anions, NO_3^- , Cl^- , Br^- , I^- , SO_4^{2-} , PO_4^{2-} , and CO_3^{2-} . The final experiment will involve the analysis of a general unknown of cations examined in the previous laboratory experiments.

Qualitative analysis has remained an important part of the laboratory experience in general chemistry for a number of years, even though the analytical methods have been replaced by sophisticated instrumental methods in practical analysis. We believe that qualitative analysis has two useful purposes: (1) It provides an ideal context for the illustration and application of the principles of ionic equilibria, such as acid-base, solubility, and complex ion equilibria, and (2) it provides a logical and systematic framework for the discussion of the descriptive chemistry of the elements. Its utility aside, analysis is fun.

ORGANIZATION OF THE SCHEME FOR QUALITATIVE ANALYSIS

Of the approximately 80 metallic elements, 24 of the more common cations are usually included in the scheme of analysis. In the abbreviated scheme presented in this and the next two experiments, we will study the separation and identification of only ten cations. This permits an extensive introduction to the more commonly employed separative techniques in only three 3-hour laboratory periods and does not require handling the dangerous and olfactorially offensive hydrogen sulfide gas, H_2S .

All qualitative schemes begin with the separation of Ag^+ , Pb^{2+} , and Hg_2^{2+} ions, as their insoluble chlorides. These ions constitute Group 1 in most schemes of qualitative analysis.

We will not analyze for any of the eight elements generally included in Group II. These divalent or trivalent elements are all located near the amphoteric or semimetal element staircase line of the periodic table.

Group III is generally separated as a mixture of hydroxides and sulfides by precipitation from a solution containing NH_3 or both NH_3 and NH_4HS . In the abbreviated scheme used here, Fe^{3+} , and Al^{3+} are first precipitated as hydroxides, and Zn^{2+} is subsequently separated as the insoluble sulfide by addition of NH_4HS or thioacetamide. We will use thioacetamide in our analysis.

Table-1 presents an overall scheme to illustrate this separation into groups. It is important for you to study the flowchart in this table so that you understand the basis for separating the cations into five groups. This will be especially true if you proceed through the analysis scheme to the **general unknown**, where you will analyze cations from all groups.

LABORATORY TECHNIQUES FOR QUALITATIVE ANALYSIS

The oft-repeated admonition *keep your lab bench neat and orderly* will pay big dividends in time saved and in fewer mistakes. Study Figure-1. Keep the bench top and the area in front of the sink clear of unnecessary equipment. Arrange conveniently the most frequently used items, such as clean

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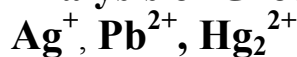
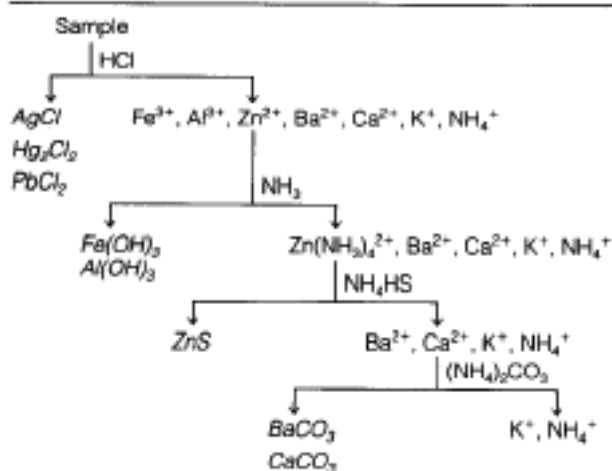


TABLE 31-1

The Abbreviated Scheme for the Separation of Ten Metal Ions



test tubes, your wash bottle, and stirring rods, polyethylene transfer pipets, and indicator test paper, laid out on a clean towel. Keep dirty test tubes and other articles in one place. Clean and rinse these at the first opportunity so that a stock of clean equipment is always ready. Label any solutions that are to be kept for more than a minute or two. **Keep your laboratory records up-to-date, and do your thinking as you work.** Rushing through experimental work without thinking about it, with the idea of understanding it later, is an ill-advised attempt at economy of time.

ESTIMATE THE VOLUME OF SOLUTIONS.

Use only the small volumes specified. You can *estimate* most volumes with sufficient precision by

counting drops (20-25 drops per milliliter) or by estimating the height of the solution in the 100-mm test tube (capacity 8 mL). Use the 10-mL graduated cylinder only when more accurately known volumes are required.

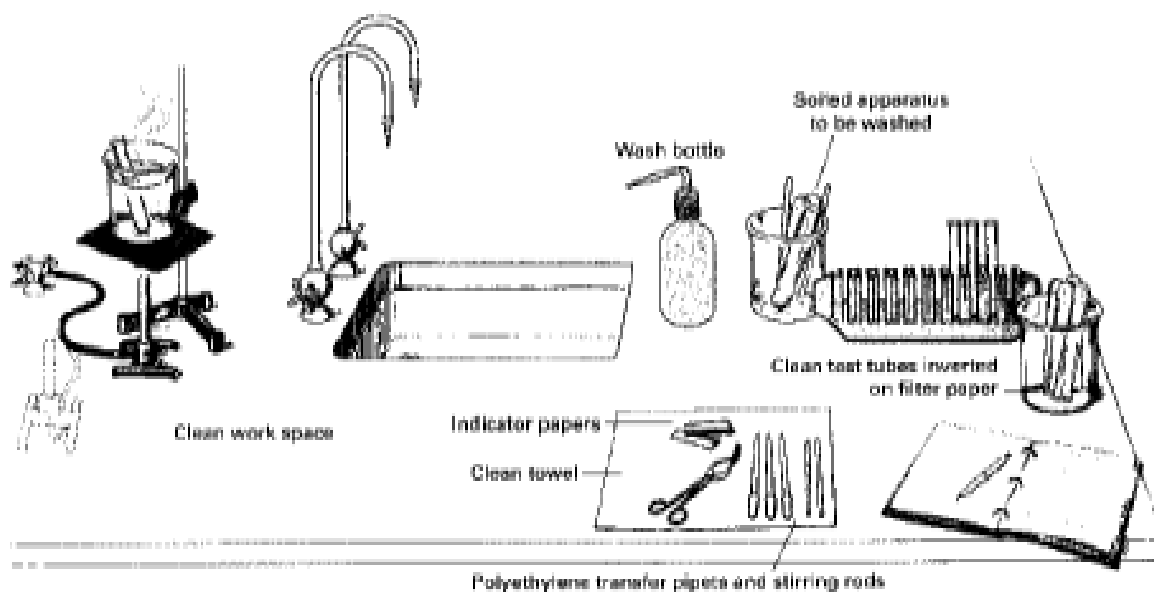


FIGURE 11-1

Keep your laboratory worktable neat and in order, with the "tools of your trade" conveniently arranged.

HANDLING OF SOLUTIONS.

Learn to be clean and efficient. Review the sections on basic laboratory equipment and procedures in the Introduction. When mixing solutions, use a stirring rod (Figure-2), or better stir content of test tube as you have been shown; do not invert the test tube with your unprotected, and possibly contaminated, thumb as the stopper. When heating solutions, avoid loss by bumping (Figure-3). Do not try to boil more than 2 mL of solution in a 10-cm test tube; transfer larger quantities to a 15-cm test tube, a small beaker, or a casserole. The safest way to heat a solution in a test tube is to immerse the tube in a beaker of boiling water.

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Ag^+ , Pb^{2+} , Hg_2^{2+}

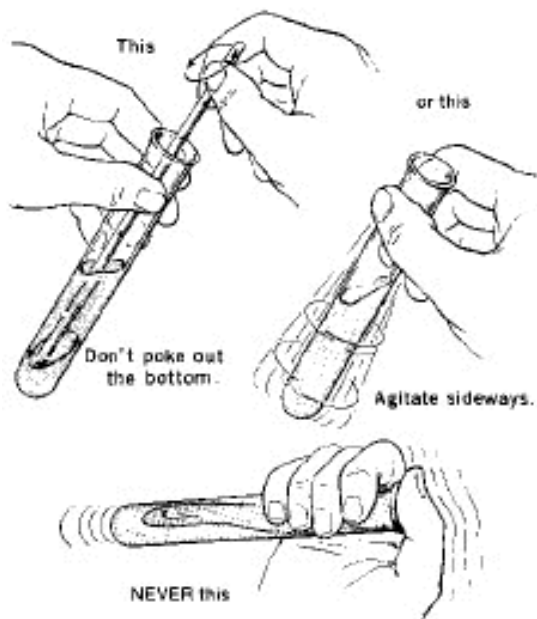


FIGURE 31-2
Learn to use good technique in mixing solutions.

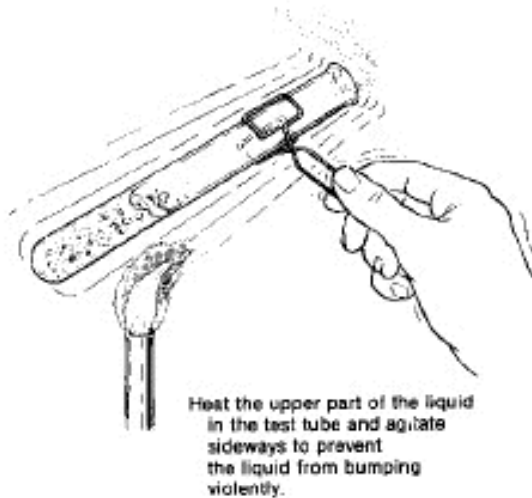


FIGURE 31-3
Use this technique when you heat a solution in a test tube.

WASHING PRECIPITATES.

When it is desirable to isolate a precipitate and free it from interfering ions in the supernatant in order to carry out further tests on it, you must first wash the precipitate. This is done by centrifuging it to the bottom of a test tube, removing the supernatant solution by carefully pouring it off or by drawing it off with a polyethylene transfer pipet, adding a few milliliters of pure water, mixing as shown in Figure-2, and re-centrifuging the precipitate. The washing can be repeated, if necessary, to remove all interfering ions.

EXPERIMENTAL PROCEDURE

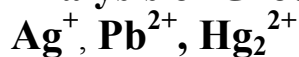
Special Supplies: Centrifuges

Chemicals: 0.1 M sodium chloride, NaCl ; 0.1 M lead(II) nitrate, $0.2 \text{ M Pb}(\text{NO}_3)_2$; 0.1 M mercury(I) nitrate, $\text{Hg}_2(\text{NO}_3)_2$; 0.1 M potassium bromide, KBr ; 1 M potassium chromate, K_2CrO_4 ; 0.1 M potassium iodide, KI ; 0.1 M silver nitrate, AgNO_3 ; 6 M hydrochloric acid, HCl ; 6 M ammonia, NH_3 ; 6 M sodium hydroxide, NaOH ; 6 M nitric acid, HNO_3 .

SAFETY PRECAUTIONS! Lead and mercury salts are toxic, and chromates are known to be carcinogenic. Silver ion is corrosive and leaves a black stain on the skin. Note that 6 M HCl , 6 M NH_3 , 6 M NaOH , 6 M HNO_3 , are corrosive. Try not to spill any Pb^{2+} , Hg_2^{2+} , Hg^{2+} , CrO_4^{2-} , Ag^+ , or 6 M acids or bases on your skin. If you do, wash them off immediately. Wash your hands thoroughly when you leave the laboratory.

WASTE COLLECTION: None of the solutions containing the ions in this experiment should be disposed of down the drain. Waste containers should be provided for all waste solutions.

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EXPERIMENTAL PROCEDURE

WEAR YOUR SAFETY GLASSES WHILE
PERFORMING THIS EXPERIMENT

1. Precipitation of Group I Ions. To gain familiarity with the analysis scheme we will first analyze a known Group I solution, made by mixing equal volumes of 0.1 M AgNO_3 , 0.2 M $\text{Pb}(\text{NO}_3)_2$, and 0.1 M $\text{Hg}_2(\text{NO}_3)_2$.

Add 2 drops of 6 M HCl to 1 ml of the known solution in a small test tube. Centrifuge the solution, being careful to place a blank test tube containing an equal volume of water in the opposite tube of the centrifuge. Add one more drop of the 6 M HCl to the solution to test for completeness of precipitation. Centrifuge again if necessary, and decant the supernatant solution from the chloride precipitate. The solution should be saved for further study if ions from other groups may be present.

2. Separation of Pb^{2+} . Wash the precipitate with 1 or 2 ml of water. Stir with a glass rod, centrifuge, and decant. Discard the decanted liquid.

Add 2 ml of distilled water to the precipitate in the test tube and place in a 250-ml beaker which is half full of boiling water. Allow the tube to remain in the boiling water bath for a few minutes, and stir occasionally with a glass rod.

Centrifuge the hot solution and quickly pour it into another test tube. Save the remaining precipitate for further study.

3. Identification of Pb^{2+} . Add one drop of 6 M acetic acid and a few drops of 1 M K_2CrO_4 to the solution from 2. If Pb^{2+} is present in the solution, a yellow precipitate of PbCrO_4 will form.

4. Separation and Identification of Hg_2^{2+} . Add 10 drops of 6 M NH_3 to the precipitate from 2 and stir thoroughly. Centrifuge the solution and decant. A gray or black precipitate, produced by reaction of Hg_2Cl_2 with ammonia to produce metallic mercury, will establish the presence of Hg_2^{2+} .

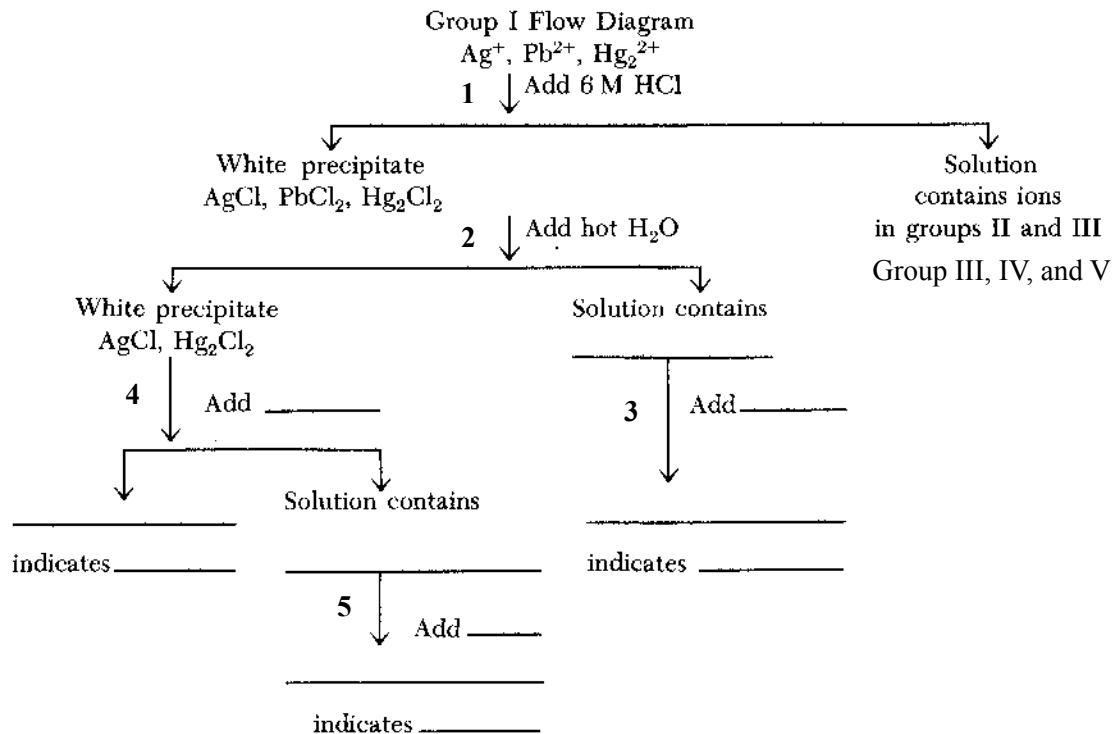
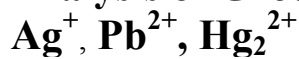
5. Identification of Ag^+ . Add 6 M HNO_3 to the solution from 4 until it is acidic toward litmus paper. Test for acidity by dipping the end of your stirring rod in the solution and then touching it to a piece of blue litmus paper (red in acid solution). If Ag^+ is present in the acidified solution, a white precipitate of AgCl will form.

6. When you have completed the tests on the known solution, obtain an unknown and analyze it for the possible presence of Ag^+ , Pb^{2+} , and Hg_2^{2+} .

FLOW DIAGRAMS

It is possible to summarize the directions for analysis of the Group I cations in what is called a flow diagram. In the diagram, successive steps in the procedure are linked with arrows. Reactant cations or reactant substances containing the ions are at one end of each arrow and products formed are at the other end. Reagents and conditions used to carry out each step are placed alongside the arrows. A partially completed flow diagram for the Group I ions follows:

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You will find it useful to construct flow diagrams for each of the cation groups. You can use such diagrams in the laboratory to serve as a brief guide to procedure, and you can use them to directly record your observations on your known and unknown solutions.

Flow diagrams, or flowcharts are provided for the next two experiments and are left for you to complete as a part of your notebook entry.

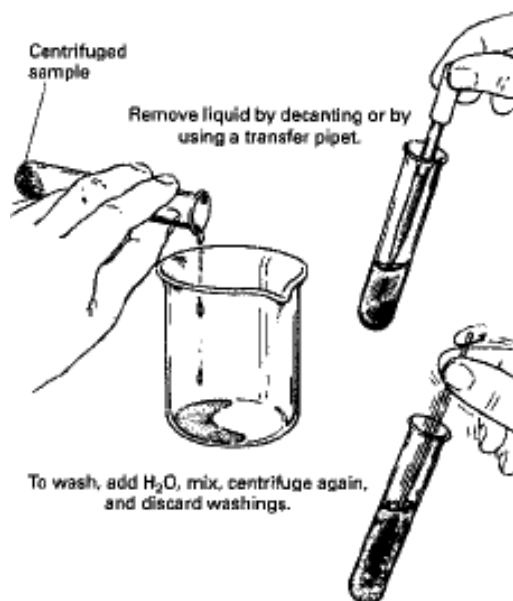
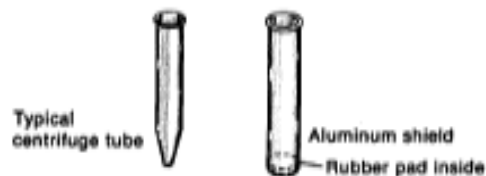
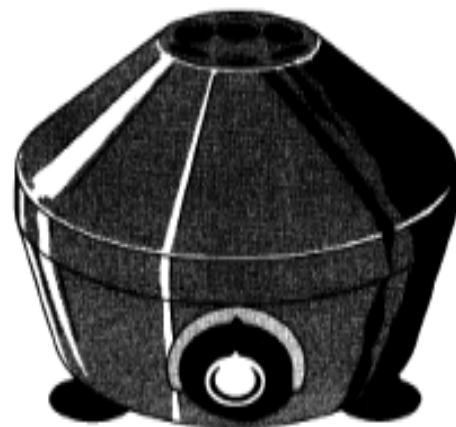


FIGURE 31-4



Opposite pairs of tubes should be filled with equal amounts of liquid to prevent excessive vibration.

Name: _____

Date: _____

Lab Partner: _____

Lab Section: _____

Lab Report: Qualitative Analysis of Group 1 Cations

In the space provided below construct a flow chart for the analysis of your unknown. Indicate on the flow chart whether the test for each ion is positive or negative.

Unknown number _____

Ions present in your unknown _____