

Experiment 12: Qualitative Analysis of Cations

Pre-Laboratory Assignment

The pre-lab assignment for Part A of the experiment is to complete the flow chart and answer the question on page 10 of this document. There is **no** pre-lab assignment for Part B.

Objective: To separate different cations in aqueous mixtures using selective precipitation and to confirm their identities using chemical tests.

Introduction

The Eagle Art Studio and Print Shop had finally found an appropriate space to rent near the center of town. They were able to move into a large vacant room overlooking the baseball diamond and playground of Milford Park. However, the location of an art studio near the park had some of the town residents worried. What if the paints, inks and ceramic pigments that the artists used were being poured into the sinks? Could the metallic components responsible for the colors get into the groundwater?

The Town Council contacted the Massachusetts Water Resource Authority, which scheduled tests to be run on the water coming out of the studio. The owners of the shop decided they should do some of their own tests on samples from the sink traps in the building in order to determine what metallic cations their employees might be discarding into the drains.

Principles of the Qualitative Analysis of Cations

The process of finding out *what* compounds are contained in a sample is called *qualitative analysis*. The process of finding out *how much* of a compound is contained in a sample is called *quantitative analysis*. You have used several *quantitative* analysis techniques, such as titration and spectrophotometry. During the next three weeks, you will use *qualitative* analysis techniques in order to determine what metallic cations are contained in aqueous solutions that are provided for you. These techniques will allow you to both separate the cations in the mixture as well as to identify them.

The various salts of the cations that you will be studying have varying solubilities in water. The differences in solubilities of these salts can be exploited in such a way as to allow for separation of the cations. As an example, let's examine the cations calcium, Ca^{2+} , and sodium, Na^+ . Calcium chloride is readily soluble in water, while calcium hydroxide is highly insoluble in water. By contrast, sodium chloride and sodium hydroxide are both readily soluble in water. An aqueous solution which contains a mixture of calcium chloride and sodium chloride can be treated with an aqueous solution that contains hydroxide ions. The result of such treatment will be the formation of a solid precipitate that is composed of insoluble calcium hydroxide. The sodium hydroxide, on the other hand, remains dissolved in the water. The solid material that contains the calcium ions can be separated from the aqueous solution containing the sodium ions using a technique such as filtration.

In summary, the addition of an appropriate chemical reagent to an aqueous mixture of cations can selectively cause one or more of the cations to form a solid precipitate while one or more of the cations will remain dissolved in the water, thus

allowing for separation. (Pages 749-754 in Tro also discuss principles involved in qualitative analysis.)

General Procedures for the Qualitative Analysis of Cations

Avoiding Contamination

As you follow the procedures for separating and identifying the cations in a mixture, it will be extremely important to avoid contamination of the samples and chemical reagents at all times. The presence of a contaminant that contains a cation will lead to a false positive result; therefore, it is critical that all glassware be thoroughly cleaned before it is used and should remain clean throughout the procedure. Laying a glass stirring rod on a dirty lab bench, for instance, could lead to contamination. Touching the tip of a medicine dropper to the side of a test tube could cause contaminants to be picked up and transferred to another solution. In addition, all water used for these procedures must come from the plastic, white faucets in the lab that deliver de-ionized water. Tap water from the regular faucets contains a wide variety of ions and could result in misleading observations.

Equipment and Chemicals

The tests that you will perform to identify the cations after they have been separated require only very small amounts of sample. Therefore, you will work with the smallest size test tubes available (10 x 75 mm), thin glass stirring rods and medicine droppers. Rather than measuring volumes of liquids with a graduated cylinder, it will be easier to simply count the number of drops of liquid dispensed from a medicine dropper. In general, it is safe to assume that *20 drops from a medicine dropper is equivalent to 1 mL of solution*. You will usually be told exactly how many drops to add in any given step of the procedure. As mentioned previously, it is very important that the medicine droppers **never** become contaminated, for instance, by allowing the tip to touch either the surface of a solution or the side of a test tube.

The chemical reagents for the qualitative analysis procedures are aqueous solutions that are contained in dropper bottles. The caps of these bottles are labeled. Do not put the wrong dropper into a bottle, or the entire contents of the bottle will become contaminated! When you have finished using the bottle, screw the cap back on *tightly*. If the cap is not on tight, the next person to grab it by the dropper will knock the bottle over. In addition, some of the water will evaporate if the cap is not on tight, and this will alter the concentration of the solution.

Mixing

After a reagent has been added to a solution in a test tube, it is very important that the solutions are stirred together thoroughly. Reactions cannot proceed to completion unless the reactants come into intimate contact with each other. Use a *thin* stirring rod to mix the liquids so that the contents of the test tube do not overflow. Of course, the stirring rod must be rinsed well with de-ionized water before being used.

Checking Acidity/Basicity

In many cases during the separation of cations, an acid or base solution is added to a sample until the pH of the solution becomes either acidic or basic. In these instances, litmus paper is used to monitor the pH. A drop of the solution being tested is removed from the test tube using a glass stirring rod. The rod is touched to the litmus paper, and

the color of the paper indicates whether the pH is basic (blue) or acidic (red). The litmus paper must never be placed directly into the solution! It is possible to use litmus paper to observe if a solution is weakly acidic or basic as opposed to strongly acidic or basic. A strong acid or base will turn litmus paper a more intense color than will a weak acid or base.

Forming, Separating and Washing Precipitates

When an appropriate chemical reagent is added to a solution containing a mixture of cations, a precipitate will form that is composed of the insoluble salt(s) of one or more of the cations. This solid precipitate can be separated from the aqueous solution, which contains the soluble salt(s) of the remaining cations, by filtration; however, a more convenient technique for the separation of a solid from a liquid is centrifugation. A test tube containing the mixture is placed in a centrifuge, which spins the mixture at a very high speed. The resulting centrifugal force packs the solid material tightly into the bottom of the test tube. The liquid supernatant can then be easily poured away, or *decanted*, from the solid. Read about Using a Centrifuge in TECH Section VI.

Before the liquid supernatant is decanted from the solid material, it is a good idea to check for complete precipitation. After centrifuging the mixture, add one or two more drops of the reagent which caused precipitation to occur. Watch the supernatant carefully to see if more precipitate forms. If no more precipitate forms, then precipitation is complete and the supernatant may be poured off. If more solid does appear in the supernatant, add another drop or two of the reagent solution, thoroughly stir the contents of the test tube, and place it back in the centrifuge for two minutes. The process of checking for complete precipitation should continue until no solid appears in the supernatant upon addition of the reagent.

After the liquid has been decanted from the solid, a small amount of this solution will remain behind in the test tube with the solid. In order to completely remove this liquid and any contaminants that it contains, the precipitate is washed with water. Ten to fifteen drops of water are added to the test tube, and the mixture of solid and liquid is thoroughly stirred with a glass rod. The test tube is placed in a centrifuge for two minutes, then the water is decanted away from the solid and may be disposed of down the drain. Solids are usually washed two times before proceeding to the next step in the procedure.

Heating Solutions

Occasionally, a step in a qualitative analysis procedure will require that a solution or mixture be heated. A water bath usually provides a high enough temperature. Place about 150 mL of water in a 250 mL beaker and heat it on a hot plate. A metal *beaker cover* with four holes in it is available in your drawer. This metal plate can be placed on top of the beaker, and 10 x 75 mm test tubes can be inserted into the holes such that the bottom of the test tube is positioned in the middle of the boiling water. It can take some time for the water to reach the boiling point, so if you know you will require a water bath at some point in the procedure, you should set the water on a hot plate at the beginning of the lab period.

Labeling

During the qualitative analysis procedures, you will be manipulating a large number of test tubes with a variety of contents. It is vital that everything be clearly and properly labeled. Solutions and solids can be inadvertently discarded if test tubes do not

have accurate labels. Also, before you place one of your test tubes in the centrifuge with other students' test tubes, you must label it with your name.

Laboratory Notebook

As always, you must record very complete and descriptive observations in your lab notebook throughout the qualitative analysis procedures. You might find it useful to organize your observations in a table. Color changes, the presence or absence of cloudiness and the formation of bubbles are all relevant observations that must be carefully noted. You should record the color of solutions *before* they are added to each other, as well as what happens after they are mixed together. Remember that there is a difference between the terms *clear* and *colorless*. To say that a liquid is "clear" indicates that no solid material is present, while the absence of color is best described by the word "colorless". For instance, if two non-colored solutions are mixed together and a white precipitate forms, the correct observation is a "colorless and cloudy" mixture.

Your TA will collect the carbon copies of your notebook pages at the end of each of the qualitative analysis lab periods. Because you will be performing the qualitative analyses over three lab periods, it is especially important that you record completely what you did and what you observed in lab each day. You will need to refer to observations from the previous lab periods in order to successfully complete the analyses.

Hazardous Chemical Byproducts

Some of the chemical reagents and cations that you will work with during the qualitative analysis procedures are toxic. These materials present a hazard to the environment and must be collected in the **Laboratory Byproducts** jars. Those chemicals that are not hazardous may be safely poured down the drain. Read carefully the instructions provided for each experiment, and listen to your instructor's pre-lab talk to learn which materials may be disposed of in the sink and which must be collected in a Byproducts jar. Ask your TA if you have any questions regarding the proper disposal of a chemical.

Safety Precautions

The standard safety rules must be followed when carrying out the qualitative analysis procedures. You must wear both a lab apron and chemical splash goggles. Some of the reactions that occur will generate hazardous fumes such as ammonia, so it is prudent to work in the fume hood whenever possible. Read the labels of reagent bottles carefully to be sure you have chosen the right chemical and the right concentration.

The Analyses

In the first week of the qualitative analysis sequence, you will be given explicit instructions to follow in order to separate the cations Ag^+ , Fe^{3+} and Co^{2+} and confirm their presence (Part A). In the second and third weeks, you will have to devise your own scheme for separating the cations ZrO^{2+} , Ni^{2+} , Pb^{2+} and Al^{3+} (Part B). In both Parts A and B, you will first be provided with a solution that contains all of the cations in question. After you have successfully followed the procedure to separate and confirm their presence, you will be given an "unknown" solution that contains one or more of the indicated cations. By following the same procedure that you used for the "known" solution, you will be able to identify which of the cations are present in the "unknown" solution.

Part A. Analyzing Solutions for Silver (I), Iron (III) and Cobalt (II) Ions

The first step in the separation of these three cations involves the precipitation of the silver ion as the insoluble silver chloride salt. This precipitation is accomplished simply through the addition of hydrochloric acid.

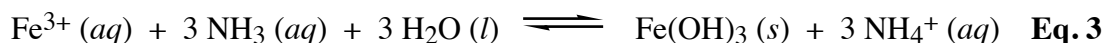


Since neither iron (III) nor cobalt (II) forms an insoluble chloride salt, the silver can then be separated from the other two cations by centrifuging the test tube and decanting the supernatant. A test is next performed to confirm the presence of silver in the precipitate that remains in the test tube. First, ammonia is added, which results in dissolution of the silver (I) compound.

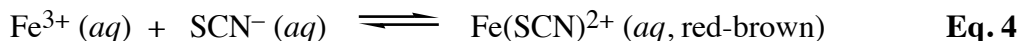


Adding nitric acid will shift the equilibrium to the left as the acid reacts with the ammonia, NH_3 , causing the silver ion to re-precipitate as silver chloride.

The supernatant that was decanted earlier contains both Fe^{3+} and Co^{2+} . Addition of ammonia to this solution causes the iron (III) ion to form an insoluble hydroxide and precipitate out of solution.



Centrifugation and decantation leaves $\text{Fe}(\text{OH})_3$ solid which can be dissolved in hot hydrochloric acid. There are two confirmation tests for iron (III), and you will perform both. In the first, addition of potassium thiocyanate solution produces a red-brown color if Fe^{3+} is present.

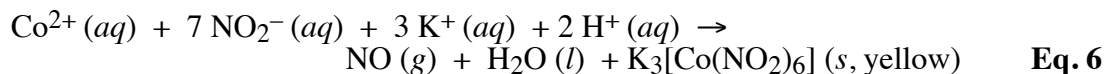


In the second test, ammonia is first added until the solution is only weakly acidic, and this is followed by the addition of potassium ferrocyanide, $\text{K}_4[\text{Fe}(\text{CN})_6]$, solution. The dark blue solid that appears when iron (III) is present is a dye known as Prussian blue.

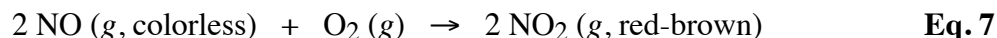


A suspension of this compound is used in some blue inks.

The presence of the cobalt ion, which now remains in the decanted supernatant solution, can be confirmed in a simple test. The basic solution is made strongly acidic with the addition of hydrochloric acid. Addition of a solution of potassium nitrite, KNO_2 , will produce an insoluble yellow compound, potassium hexanitritocobaltate (III).



The reaction in Eq. 6 produces nitric oxide, NO , which is a colorless gas. Nitric oxide reacts with oxygen in the air to produce nitrogen dioxide, NO_2 , which may be visible as a red-brown gas.



Procedure

Make a table in your notebook similar to that shown on page 9 *before* coming to lab. Enter all your observations in this table.

You will dispense 2 mL of a solution that contains Ag^+ (**toxic**), Fe^{3+} and Co^{2+} into a test tube. To use the bottletop dispenser, refer to the picture attached to the bottle. Raise the piston slowly and evenly to the stop. Place a 13x100 mm test tube under the discharge tube, then press down slowly and evenly on the piston. Never touch the volume-setting knob on the side of the piston casing!

Transfer 15 drops of the solution in the test tube to a smaller, 10x75 mm, test tube using a medicine dropper. Add 6 drops of 6 M HCl solution (**corrosive**) to the 15 drops of the cation solution to bring about precipitation. Be sure to stir (with a clean stirring rod) the contents of the test tube. Centrifuge the test tube for 2 minutes. Add one drop of 6 M HCl to the test tube and carefully observe the supernatant. If more precipitate is formed upon this addition, add another drop or two of HCl and centrifuge again. Re-test the solution for complete precipitation.

Confirming the presence of Ag^+ ion

When it has been determined that precipitation of silver chloride is complete, decant the supernatant into a clean test tube, label it and set it aside. Wash the precipitate that remains in the test tube by adding 10-15 drops of water to it. Stir the precipitate well and centrifuge the test tube. Decant and discard the supernatant. Repeat this procedure to wash the precipitate one more time. Add 8 drops of 6 M NH_3 solution (**corrosive, irritant, strong fumes**) to the washed precipitate and stir well. Record your observations. Add 6 M HNO_3 solution (**corrosive, strong oxidant**) with mixing until the solution is acidic when tested with litmus paper. Record your observations.

Important! Discard all precipitates and solutions that you suspect contain silver into the **Laboratory Byproducts Jar** labeled "Silver". Do not dispose of silver down the sink!

Separating and confirming the presence of Fe^{3+} ion

Add a sufficient amount of 6 M NH_3 solution to the supernatant that was set aside earlier until the solution is basic when tested with litmus paper. **Stir well and be sure the solution is strongly basic!** Centrifuge the test tube and test for complete precipitation. When it has been determined that the precipitation of iron(III) hydroxide is complete, decant the supernatant into a clean test tube, label it and set it aside. Wash the remaining precipitate with water. Add 10 drops of 6 M HCl to the washed precipitate. Heat the mixture in a boiling water bath to dissolve the precipitate, if necessary. When the precipitate has dissolved, test with litmus paper to be sure it is strongly acidic. Separate the solution into two approximately equal portions. To one portion, add 3 drops of 0.1 M KSCN solution and record your observations. To the other portion, add 6 M NH_3 until the solution, which was strongly acidic, now tests only weakly acidic. If the solution becomes basic, add 6 M acetic acid solution dropwise until it is weakly acidic. Add 3 drops of 0.1 M $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution and record your observations.

Confirming the presence of Co^{2+} ion

To the supernatant that was set aside, add 6 M HCl until the solution tests acidic. **In a fume hood (the gas generated is toxic!),** add 6 drops of 6 M KNO_2 solution

(oxidizer, irritant), mix well and record your observations. When the evolution of gas has subsided (this may require several minutes), centrifuge the test tube and discard the supernatant so that the precipitate and its color can be clearly observed. The appearance of a yellow precipitate confirms the presence of Co^{2+} .

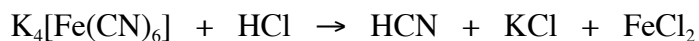
Note: All solutions and precipitates that do **not** contain silver may be disposed of in the sink.

Obtain from your instructor an unknown solution that contains one or more of the cations Ag^+ , Fe^{3+} and Co^{2+} . Repeat the above procedure using 15 drops of this solution. Record all your observations, then fill in the data sheet on page 11 and hand it in to your TA before leaving the laboratory.

Wash your hands thoroughly before leaving the lab.

Questions (the answers to these questions must be handed in to your TA at next week's lab period)

1. If potassium ferrocyanide, $K_4[Fe(CN)_6]$, is added to a strongly acidic solution, toxic hydrogen cyanide, HCN, gas is produced. Balance the following equation, which represents this reaction:

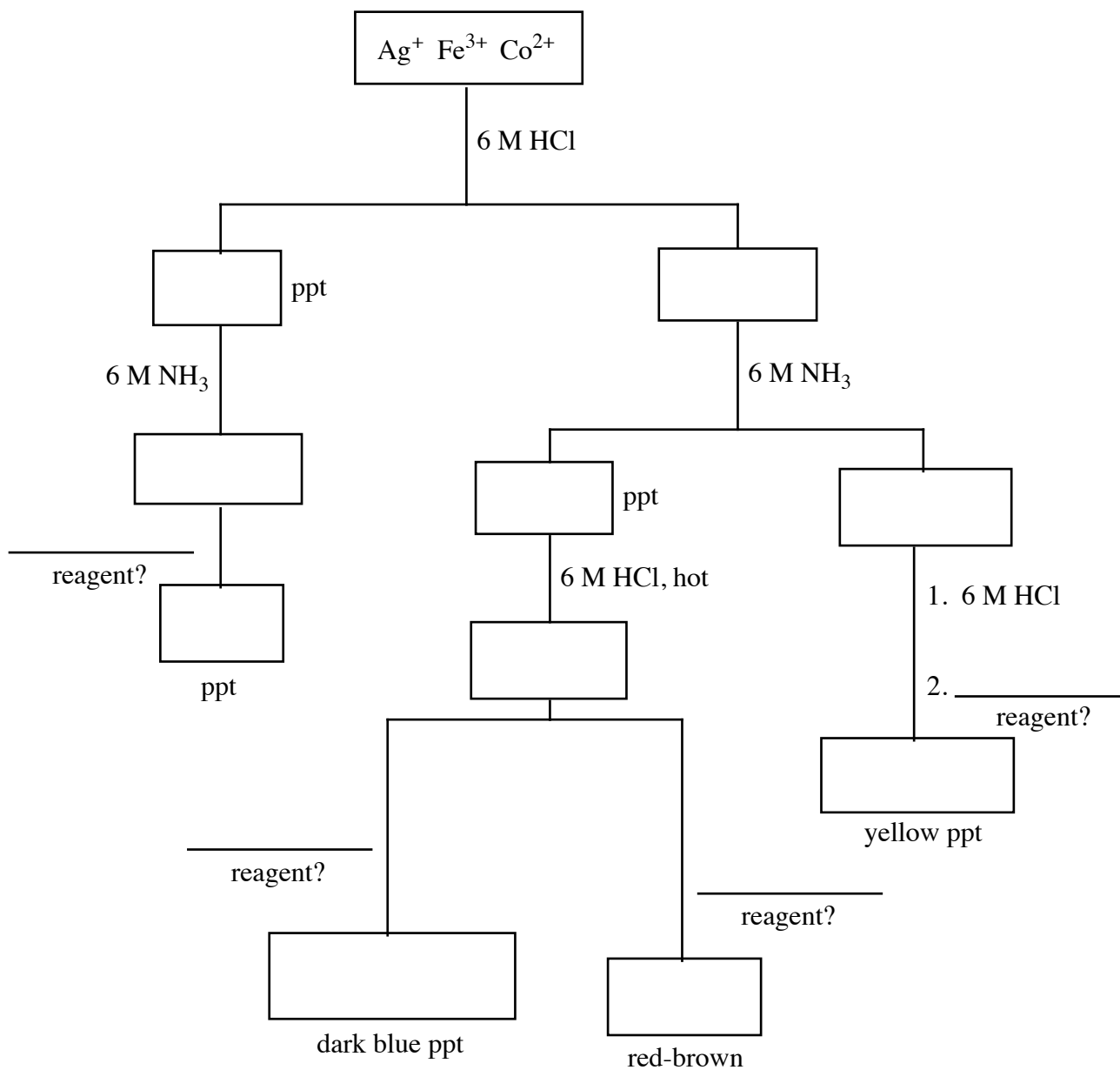


Is this reaction an example of a redox reaction? Why or why not?

2. What will happen if ammonia is added to a mixture of Ag^+ , Fe^{3+} and Co^{2+} ? Describe the subsequent steps that could be performed to separate the three cations.
3. After the silver ion is precipitated as silver chloride, the precipitate is washed with water. Why is this washing performed, and what *exactly* is being washed away? Similarly, the iron (III) hydroxide precipitate is washed with water. What is being washed away in this case?

Pre-Laboratory Assignment for Part A.

1. Complete the following flow chart. [Note: ppt = precipitate]



2. List the hazardous chemicals used in this experiment and the hazards associated with each. Which chemicals need to be disposed of in a **Laboratory Byproducts Jar**?

Name _____

TA _____

Date _____

Data Sheet for Part A

Unknown Identification Number _____

Cations found _____

Part B. Analyzing Solutions for Lead (II), Nickel (II), Aluminum (III) and Zirconyl Ions

NOTE: There is no pre-laboratory assignment for this part of the experiment.

You will be provided with a “known” solution that contains the following four cations: ZrO^{2+} (this is a complex ion, similar to NH_4^+), Ni^{2+} (**toxic!**), Pb^{2+} (**toxic!**) and Al^{3+} . You will design your own scheme to separate these cations from each other and then confirm their presence by confirmation tests. You will use the same techniques that you employed in the separation and confirmation of silver, iron and cobalt cations.

Separation of the Ions

Three reagents that are quite useful in the separation of these four cations are hydrochloric acid, sodium hydroxide and ammonia. Begin by determining which cations are soluble in which reagent and which are insoluble. Solutions of each of the individual cations will be provided for you along with 6 M solutions of the three reagents. Add 3 drops of the reagent solution to 3 drops of the cation solution and examine the resulting mixture for a precipitate. Record all your observations and summarize them in a table similar to the following in your notebook, using the letters *ppt* for *precipitate* and the letter *s* for *soluble*.

Cation	NaOH	HCl	NH ₃
ZrO ²⁺			
Ni ²⁺ (toxic!)			
Solubility of nickel precipitate(s)			
Pb ²⁺ (toxic!)			
Al ³⁺			

Important Note!

Test the solubility of any precipitates that appear for nickel in the other two reagents. For instance, if you see a precipitate when one of the reagents (NaOH, HCl or NH₃) is added to the nickel solution, centrifuge the test tube, decant the supernatant, wash the precipitate once with water and add 3 or 4 drops of one of the other two reagents to this precipitate. Record your observations in the table you have prepared. Repeat the procedure (you'll need to start with a new sample of the nickel solution to precipitate the solid), this time adding 3 or 4 drops of the other reagent solution to the washed precipitate.

You must develop your own scheme for separating and identifying the cations. There are several different possible procedures that can be used for carrying out this separation, and no one way is “correct”. You may find a flow chart to be useful in summarizing the steps of your procedure. [Note: Your TA will take into consideration how much assistance you require in devising your scheme when s/he assigns a grade.]

Begin with 15 drops of either the known or unknown solution as you did in the previous analysis (Part A). Use anywhere from 6 to 12 drops of the desired acid or base reagent to precipitate the cations, and remember to check for complete precipitation. Thoroughly wash any precipitates that will be used for further analysis. Use anywhere from 6 to 12 drops of the desired acid or base reagent to dissolve precipitates. After adding the desired reagent, test the solution with litmus paper to be sure that it is either strongly acidic or basic.

Another important note!

When precipitating the lead cation, add the appropriate reagent, then place the test tube in *ice* for 5 minutes.

Confirmation Tests

The following tests should be performed to confirm the presence of the cations *after* they have been completely separated from each other. Each test can also be performed using a known solution of the individual cation in order to observe a positive test result (this is called a *control*). A negative test result can be observed by performing the test on water (this is called a *blank*).

Zirconyl, ZrO^{2+}

Dissolve a precipitate that you suspect contains zirconyl in 6 M HCl, *or* add enough HCl to a solution that you suspect contains zirconyl to make it acidic (test with litmus paper). *In a clean test tube*, place 2 drops of Alizarin Red solution. Add 2 drops of the acidic solution of zirconyl to the Alizarin Red solution. Check that the solution is still moderately acidic. Heat the solution for 2 minutes. The appearance of a red-violet color indicates the presence of ZrO^{2+} .

Nickel, Ni^{2+}

Dissolve a precipitate that you suspect contains nickel in 6 M HCl, then add 6 M NH_3 until strongly basic, *or* add enough NH_3 to a solution that you suspect contains nickel to make it strongly basic (test with litmus paper). Add 1 drop of 1% dimethylglyoxime (DMG) solution. The appearance of a cherry red precipitate indicates the presence of Ni^{2+} . Nickel is toxic and must be disposed of in the appropriate **Laboratory Byproducts Jar**.

Lead, Pb^{2+}

Add 10 or more drops of water to a precipitate that you suspect contains lead. Heat to dissolve the solid. Add 2 drops of acetic acid and 4 drops of 0.1 M potassium chromate, K_2CrO_4 , solution (**toxic!**). The formation of a bright yellow precipitate confirms the presence of Pb^{2+} . This precipitate is toxic and must be disposed of in the appropriate **Laboratory Byproducts Jar**.

Aluminum, Al^{3+}

Dissolve a precipitate that you suspect contains aluminum in 6 M HCl, *or* add enough HCl to a solution that you suspect contains aluminum to make it acidic (test with litmus paper). Add 2 drops of 0.1% aluminon solution, then add 6 M NH_3 until the solution tests basic with litmus paper (stir well!). If no precipitate forms (the solution is clear), Al^{3+} is not present. If a red-pink

precipitate forms (the solution is cloudy), centrifuge the test tube and decant the supernatant. Add 3 drops of 6 M NaOH to the solid. If Al^{3+} is present, the precipitate will dissolve and a clear magenta solution will form. If the precipitate does *not* dissolve in NaOH, ZrO^{2+} is probably present, and possibly Al^{3+} as well.

More Important Notes!

Both lead and chromium are toxic. Any solutions or precipitates that you suspect contain lead and/or chromium **must** be disposed of into the **Laboratory Byproducts Jar** labeled "Lead and Chromium". Also, any solutions or precipitates that you suspect contain nickel **must** be disposed of into the **Laboratory Byproducts Jar** labeled "Nickel".

Wash your hands thoroughly before leaving the lab.

You will work on Part B for two lab periods. Analyze the known solution during the first period to confirm that your scheme works. You will be given an unknown solution at the beginning of the second period. This solution contains one or more of the four cations. Analyze your unknown solution, report the ions that you detect on the data sheet provided (p. 16) and hand it in to your TA before leaving the laboratory. You must record *all* observations that you make during both these lab periods in your lab notebook. Your TA will collect the carbon copies of your notebook pages at the end of each period.

Questions

1. Write out the procedure that you devised for separating the four cations in a step by step manner so that someone else performing the experiment could follow it.
2. Write balanced molecular equations for the formation of any precipitates that appeared upon addition of HCl or NaOH when testing the solubilities of the cations (refer to your solubility table). [Use NO_3^- as the anion in the formulas for the metallic compounds.]
3. When precipitating the lead cation, you were told to place the test tube in ice after adding the appropriate reagent. Suggest a possible reason for this instruction. [**Hint:** See section 12.4 in Tro.]

Name _____

TA _____

Date _____

Data Sheet for Part B

Unknown Identification Number _____

Cations found _____
