Introduction to Inorganic Qualitative Analysis

Introduction

In this experiment you will be introduced in a very abbreviated way to systematic methods that chemists have traditionally used to identify the cationic constituents of a mixture. In most such schemes, including this one, a sequence of precipitating agents is used to separate the original mixture into smaller groups, each of which may contain more than one constituent. Each of the smaller groups is then examined further.

The elements that you will be focusing on are eight of the twelve metallic constituents of the third long row of the periodic table: K, Ca, Cr, Mn, Fe, Co, Ni, and Zn. You will first encounter them as 0.05 M aqueous solutions of nitrate salts. During the course of the experiment some of these elements may change their oxidation states one or more times.

The scheme you will be using does not include the Cu^{2+} ion because it behaves rather unpredictably when subjected to the reagents used here to effect the separation of a mixture of these cations. In more elaborate analytical schemes the copper gets removed early on by precipitating it as the sulfide from a 0.3 M acid solution saturated with hydrogen sulfide. The sulfide ion concentration in such a solution is so incredibly low that only CuS ($K_{sp} \sim 10^{-35}$) precipitates at that point.

The first part of the experiment comprises a series of diagnostic tests in which you will determine experimentally how six of the eight salts respond to the various treatments that will comprise the overall analytical scheme. ***These tests may all be performed in a single laboratory period if you have thoroughly studied the experiment before you come to lab so that you know exactly what you will be doing and in what order.***

Safety: Gloves must be worn **at all times**. Some of the reagents used in this experiment can cause burns or other skin damage.

Procedure

Work individually on this experiment.

In order to successfully complete this experiment please adhere to the following GENERAL GROUND RULES:

1. All Glassware must be kept scrupulously clean.

2. You must not contaminate any of the reagents or test solutions. Each reagent/test solution has its own dropper which is kept in a "side car" taped to the bottle. Use the dropper to dispense what you need, then return it to its proper place. If a dropper does get contaminated, simply throw it away and replace it with a new disposable pipet.

Part I. Qualitative Analysis - Observing Reactions

During the course of this experiment you will need your own modest supplies of a few common reagents. As you study the experimental details below you can estimate about how much of each one you are going to need, and should procure only about that much from the community bottles. You can always go back for more if needed. Obtain suitable quantities of 6 M NaOH and 6 M HNO_3 and store them in clean test tubes, each equipped with its own disposable dropping pipet. In another clean test tube prepare a 3% solution of hydrogen peroxide by a 1:10 dilution of the 30% stock solution. Supply this test tube with a dropping pipet as well.

You will also need a near-boiling water bath. Make one by filling your 400 mL beaker about 1/3 full of DI water and bring it to a gentle boil. When you need to heat something up just turn the burner off to cool slightly.

Use your 800 mL beaker as a waste liquid receptacle. Whenever you are instructed to "discard" some metal ion aqueous solution, place it in the 800 mL beaker. AT THE END OF THE LAB PERIOD EMPTY IT INTO THE PROPER WASTE CONTAINER. IF THE WASTE CONTAINER IS FULL, TAKE THE FULL BOTTLE TO THE DISPENSARY AND REPLACE IT WITH AN EMPTY ONE.

Over the course of this and the following experiment you will be asked to make a great many "dropwise" additions of various reagents to various test tubes. One quite effective way to do this is as follows: Hold the test tube between the thumb and third fingers of one hand and the appropriately-filled dropping pipet in the other one. Use the tip of the index finger on your "holding" hand to keep the shaft of the dropping pipet from touching the tube wall as you lower it near to (but always above) the liquid level in the test tube. Also, try holding the test tube and dropper at about shoulder height with your elbows tucked against your rib cage to steady your arms. Crouching on the floor with your elbows on the table gets awfully tiresome.

Part A. Initial Tests: The Experimental Basis for the Separation of a Complex Mixture into sub-groups.

After each of the following steps record your observations.

Step 1. Line up six labeled centrifuge tubes in your test tube rack and to each one add 1 mL of one of the cation test solutions, **OMITTING** potassium nitrate and calcium nitrate. These two cations can be picked up in diagnostic tests that are specific for them. To each centrifuge tube in turn add 10 drops of 6 M NaOH drop-wise with gentle shaking (side-to side, not end-over-end) after every two drops.

Step 2. To each of the six centrifuge tubes next add 5 drops of 3% hydrogen peroxide solution, shaking after each addition. Place the centrifuge tubes in your water bath for about 3 minutes or until all bubbling ceases.

Step 3. At this point, four of the six centrifuge tubes should contain precipitates. Set the two tubes without precipitates aside for further treatment shown below in Step 1 of Part B, centrifuge the four that do, and then decant the supernatant liquids from above the precipitates into your liquid waste container.

Step 4. To each of the four centrifuge tubes that contain precipitates add 10 drops of 6 M HNO_3, shaking each tube gently to wet and re-disperse the precipitates. Put the four centrifuge tubes into your hot-water bath for 2-3 minutes.

Step 5. Remove all the centrifuge tubes from the water bath and set the "clear" ones aside for further treatment in Step 3 of Part B shown below. At this point, two of the centrifuge tubes should still contain precipitates. Treating one sample at a time, with shaking after each drop, add 3% hydrogen peroxide solution dropwise to each of the tubes containing a precipitate until the precipitate dissolves. (Five drops or less should do it.) Put the tubes into your hot water bath until all bubbling ceases. You will use these two solutions in Step #5 of Part B.

Part B. Confirmatory Tests for the Various Constituents

Step 1. One of the two centrifuge tubes that did not contain precipitates after Step 2 of Part A has a colored solution in it while the other solution is colorless. To each of these solutions add one drop of thymolphthalein indicator and then **very cautiously** add glacial acetic acid dropwise while gently shaking the centrifuge tube until the blue indicator color is just discharged.

Step 2. With separate disposable dropping pipets transfer a small quantity of the contents of each of these two centrifuge tubes to a well on your spot plate. To each of the centrifuge tubes add a few drops of 0.1 M lead nitrate solution. Record your observations. To each of the two spot plate wells add three drops of a solution of dithizone in chloroform and agitate them well. Record your observations. (Dithizone is an organic chelating agent that when combined with many transition metal cations forms intensely colored, uncharged complexes which can then be extracted into the chloroform layer.)

<u>Clean up</u>: Empty and rinse both of the centrifuge tubes into your temporary liquid waste container. With a disposable pipet remove as much of the aqueous layer as you can from each of the two spot plate wells and add the dropper contents to your liquid waste container. Then rinse the two spot plate wells that now contain mostly chloroform with acetone into the dithizone/chloroform/acetone waste container found in the fumehood. The EPA requires that chloroform be disposed of in a different manner from primarily inorganic materials. DO NOT FILL UP THE DITHIZONE/CHLOROFORM/ACETONE WASTE CONTAINER ABOVE THE INDICATED LINE. This will prevent spillage of the chloroform and any inconvenient clean up procedures. WHEN THE CONTAINER IS FULL UP TO THE INDICATED LINE, GO TO THE DISPENSARY TO OBTAIN A NEW WASTE CONTAINER.

Step 3. With individual dropping pipets transfer about five drops of each of the highly-acidic "clear" solutions obtained at the end of Step 4 of Part A to different wells on one of the narrow ends of your spot plate. In turn, use a dropping pipet and a *freshly cleaned* stirrer made from a loop of nichrome wire "titrate" the contents of each of the wells with 6 M NaOH to the point where a permanent hydroxide precipitate first forms. Then add one drop of 6 M HNO_3 to redissolve the precipitate again. (At this point you should therefore have a nearly neutral solution in each well.)

Step 4. In Step 4 of part A, before the addition of 10 drops of 6 M HNO_3, one of these two solutions contained a reddish-brown precipitate. To that well add two drops of potassium thiocyanate (KSCN) test reagent dropwise. Record your observations. To the second well add five drops of dimethylglyoxime (dmg) test reagent and then one or two drops of 6 M ammonia (aq). Record your observations. [If time permitted you could demonstrate to your own satisfaction that the tests you have just conducted are specific confirmatory tests for the two ions in question. Thus, at some point in the analysis of a mixture where these species could both be present in the same strongly acidic solution, putting some of it into two different wells of a spot plate, neutralizing their contents as above, and performing one of these tests on each of the wells will confirm or deny the presence of that element in the original mixture.]

<u>Clean up</u>: Hold your spot plate vertically about 1.5" above the mouth of your liquid waste container, test-wells end down, and with a gentle stream from your squeeze bottle wash away as much of the contents of the three wells as you can. Then use moist followed by dry "Kimwipes" to scrub out and dry the spot plate. You may dispose of the "Kimwipes" in the crocks on the lab bench. Pour as much as you can of any of the solutions that still remain in the original Step 3 centrifuge tubes into your liquid waste container and then rinse them out with a few mL of water from your squeeze bottle, adding the rinse water to the waste container. After that you can wash these centrifuge tubes at the sink as usual.

Step 5. Put a few drops of each of the two solutions from Step 5 of Part A into adjacent wells on your spot plate. Use a small scoop (made by slicing off the thick part of the shaft of a disposable pipet at about a 30^{o} angle) to add a slight excess of solid sodium bismuthate, $NaBiO_3$, to each well. Mix the contents of each well with a clean nichrome wire stirrer, and then let the excess solid settle out. (Don't forget to *clean* the wire off along the way so that you don't contaminate one well with the contents of the other.) Wait a few minutes until you are convinced no other changes are going to occur and record your observations.

Step 6. To each of the centrifuge tubes containing the rest of the two solutions from Step 5 of Part A add an equal volume of 4 M potassium acetate solution, about 0.2 gram of solid potassium nitrite (use a mini-scoop), seal the tube with your **gloved** finger, and shake it vigorously up and down. Record your observations. (There is nothing here that is really harmful--you should be able to convince yourself that the solution is buffered at about pH 5--but why take chances?)

Clean up: Follow the directions given in Clean up of Steps 3 and 4 of Part B for cleaning your spot plate. At this point you have nearly finished Part I of this experiment and you can therefore empty the contents of all your existing centrifuge tubes into your liquid waste container Rinse everything out with a few mL of water and then use the sink to finish cleaning your glassware.

Step 7. Step 1 of Part A did not include either potassium or calcium. The potassium ion forms an insoluble precipitate with the tetraphenylborate monoanion $[(C_6H_5)_4B^-]$. No other cation ion of interest here does so. You can therefore easily determine whether or not potassium ion is present in an unknown mixture by simply putting a few drops of the the solution of interest into a well of your spot plate, adding a drop or two of sodium tetraphenylborate solution, and looking for the formation of a precipitate. If one does form you can further confirm the presence of potassium by doing a flame test on some of the precipitate scooped up in a tiny loop in your nichrome wire.

You can form such a loop by bending one end of the wire around the tip of a pencil. You will also want to take a few tight turns around the blunt end of the pencil with the other end of the wire so you will have a way to manipulate it when it is white-hot. After you prepare the wire and before you attempt a flame test you must clean the "business end" of the wire thoroughly by rinsing it in a test tube containing 6 M HCl and then inserting it into a Bunsen burner flame just above the tip of the blue cone. You may have to resort to cleaning it in 12 M HCl if the more dilute solution is ineffective in producing a colorless flame after several dippings.

The sodium ion imparts a brilliant yellow color to a flame that, absent some appropriate action, would totally obscure the delicate violet color of a potassium flame. Fortunately, cobalt-blue glass absorbs sodium radiation quite effectively, so viewing a flame through such glass will allow the potassium flame to be observed.

You should take a few drops of the potassium nitrate test solution and confirm all of these statements.

Clean up: Wash the contents of the spot plate into your liquid waste container and clean up the plate with moistened and then dry "Kimwipes" as usual.

Step 8. The calcium ion forms a rather insoluble precipitate with the oxalate ion ($C_2O_4^{2-}$) while many of the transition metal ions of interest here form soluble oxalate complexes if the free oxalate ion concentration in the solution is high enough. Put 1 mL of each of the test solutions (except for KNO_3) into separate test tubes and to each of them add 5 drops of 0.2 M potassium oxalate solution, shaking after the addition of each drop. Record your observations. Pay particular attention to what you see when the drops first hit the solutions.

Part I Qualitative Analysis – Post Laboratory Assignment – Due before beginning Part II. To be completed on-line.

On the basis of your observations in Part I of this experiment you should be able to fill in the blanks and answer questions 1 – 7 posed on the following two pages. Questions 1 – 3 include procedures that comprise the sequence of events that you will follow to separate a complicated mixture into smaller groups for identification purposes. The narrative statements for these three questions provide fairly detailed directions for treating your actual unknown. In Questions 4 – 7, you are really being asked to formulate your own procedures for performing the necessary confirmatory tests once the major group separations have been made.

Between the first and second lab periods devoted to qualitative analysis please COMPLETE THE ON-LINE POST LABORATORY EXERCISES FOR WEEK 1. The questions you will answer on line are shown below as questions 1 – 7. If you have completed the on-line exercises for week 1 of this laboratory your TA will provide you with a blank "flow chart," which is a kind of road map through the experiment. NOTE: You must complete the on-line exercises in order get the "flow chart" needed for the 2nd day of the experiment.

Part I Qualitative Analysis – Post Laboratory Questions. To be completed on-line. Record the correct answers here while you do the on-line exercise and bring these answers to lab class with you.

Question 1. An unknown solution could contain any or all of the following cations: K^{+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}. A 1 mL portion of the unknown is treated with 2 mL of 6 M NaOH, added a few drops at a time with shaking. Immediately thereafter 10 drops of 3% hydrogen peroxide are added dropwise with shaking, and the centrifuge tube is then heated for a few minutes in a water bath until bubbling ceases.

The resulting conglomerate is then centrifuged and the supernatant liquid is decanted off and saved. (Although you have not demonstrated these facts for yourself, Ca^{2+} will be precipitated as the hydroxide at this stage and K^{+} will remain in the decanted liquid.)

At this stage of the experiment the elements that could be found in the decanted liquid are:

_____ ______ ______ _______ _______ _______ _______ _______ _______

The elements that could be found in the remaining precipitate are:

_____ ______ ______ _______ _______ _______ _______ _______ ________

Question 2. The precipitate from Question 1 is washed twice, first with a 1 mL portion of 1 M NaOH (you will make your own) and then with 1 mL of deionized water. Centrifuge the tube after each washing and discard the two supernatant liquids. Now treat the precipitate with 1 mL of 6 M HNO_3 and heat the centrifuge tube briefly in a water bath. The centrifuge tube is then centrifuged, and the supernatant liquid is decanted and saved. (The $Ca(OH)_2$ produced in Question 1 is acid soluble.)

At this stage of the experiment the elements that could be found in the decanted liquid are:

_____ ______ ______ _______ _______ _______ _______ _______ ________

The elements that could be found in the remaining precipitate are:

_____ ______ ______ _______ _______ _______ _______ _______ ________

Question 3. The precipitate from Question 2 is treated with 1 mL of 6 M HNO_3 followed immediately by the drop-wise addition of 3% hydrogen peroxide until the precipitate fully dissolves. The centrifuge tube is heated in a water bath until bubbling ceases.

At this stage of the experiment the elements that could be found in the resulting liquid are:

_____ ______ ______ _______ _______ _______ _______ _______

The elements that could be found in the remaining precipitate are:

_____ ______ ______ _______ _______ _______ _______ _______

Question 4. The decantate from Question 1 is neutralized with acetic acid and divided into the appropriate number of portions. How many portions? What should you do with each of them? What would be the observation if each treatment led to a positive (confirmatory) result?

Question 5. The final decantate from Question 2 is divided into the appropriate number of wells of a spot plate and tested as in Part I of this experiment. How many wells? What reagents would be required for each spot-test, and what would be the observation if each spot-test led to a positive (confirmatory) result?

Question 6. The liquid from Question 3 is divided into the appropriate number of portions and again spot tested. What reagents would be required and what would be the observation if each spot-test led to a positive (confirmatory) result?

Question 7. The original unknown solution is tested separately for the presence of potassium and calcium. How will you perform these tests?

Part I Qualitative Analysis – Post Laboratory Questions. (2nd Copy – only turn in this copy if your TA asks you for it.)

Question 1. An unknown solution could contain any or all of the following cations: K^{+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}. A 1 mL portion of the unknown is treated with 2 mL of 6 M NaOH, added a few drops at a time with shaking. Immediately thereafter 10 drops of 3% hydrogen peroxide are added dropwise with shaking, and the centrifuge tube is then heated for a few minutes in a water bath until bubbling ceases.

The resulting conglomerate is then centrifuged and the supernatant liquid is decanted off and saved. (Although you have not demonstrated these facts for yourself, Ca^{2+} will be precipitated as the hydroxide at this stage and K^{+} will remain in the decanted liquid.)

At this stage of the experiment the elements that could be found in the decanted liquid are:

_____ ______ ______ _______ _______ _______ _______ _______ _______

The elements that could be found in the remaining precipitate are:

_____ ______ ______ _______ _______ _______ _______ _______ ________

Question 2. The precipitate from Question 1 is washed twice, first with a 1 mL portion of 1 M NaOH (you will make your own) and then with 1 mL of deionized water. Centrifuge the tube after each washing and discard the two supernatant liquids. Now treat the precipitate with 1 mL of 6 M HNO_3 and heat the centrifuge tube briefly in a water bath. The centrifuge tube is then centrifuged, and the supernatant liquid is decanted and saved. (The $Ca(OH)_2$ produced in Question 1 is acid soluble.)

At this stage of the experiment the elements that could be found in the decanted liquid are:

_____ ______ ______ _______ _______ _______ _______ _______ ________

The elements that could be found in the remaining precipitate are:

_____ ______ ______ _______ _______ _______ _______ _______ ________

Question 3. The precipitate from Question 2 is treated with 1 mL of 6 M HNO_3 followed immediately by the drop-wise addition of 3% hydrogen peroxide until the precipitate fully dissolves. The centrifuge tube is heated in a water bath until bubbling ceases.

At this stage of the experiment the elements that could be found in the resulting liquid are:

_____ ______ ______ _______ _______ _______ _______ _______

The elements that could be found in the remaining precipitate are:

_____ ______ ______ _______ _______ _______ _______ _______

Question 4. The decantate from Question 1 is neutralized with acetic acid and divided into the appropriate number of portions. How many portions? What should you do with each of them? What would be the observation if each treatment led to a positive (confirmatory) result?

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Question 6. The liquid from Question 3 is divided into the appropriate number of portions and again spot tested. What reagents would be required and what would be the observation if each spot-test led to a positive (confirmatory) result?

Question 7. The original unknown solution is tested separately for the presence of potassium and calcium. How will you perform these tests?

Part II. Qualitative Analysis - A Deductive Introduction to the Analysis of an Unknown Mixture

In order for the on-line program to evaluate your unknown sample, you must enter your hyphenated number embossed on your locker to complete the on-line post-laboratory exercise. Please record your hyphenated number embossed on your locker in your laboratory room here. For example, in room 0435 Chemistry Annex one of the locker's hyphenated number reads, 0435-6-24; in room 66 Chemistry one of the locker's hyphenated number reads, 66-4-1.

Your locker's hyphenated number is _________ - _________ - _________.

Now it is time to analyze your unknown mixture. Obtain your unknown mixture from your TA. Be sure to obtain the unknown mixture that corresponds to the hyphenated number on your assigned locker. Each unknown mixture contains more than one of the metal constituents but fewer than eight.

You will more than likely find it helpful to take a few minutes before you begin to analyze your unknown to enter all the appropriate elemental symbols into the empty boxes in your blank flow-chart which you obtain from your TA. You might even want to supply some fairly detailed directions for some of the more complicated steps to avoid having to look them up when you really need them. Note that according to the blank flow chart mentioned above, one of the elements of interest here might show up in either or both of two places. The reason for this is with certain metal ion mixtures, the hydrogen peroxide might not survive long enough to attack all the oxidizable species present.

WASTE:

Use your 800 mL beaker again as a waste liquid receptacle. Whenever you are instructed to "discard" some metal ion aqueous solution, place it in the 800 mL beaker. AT THE END OF THE LAB PERIOD, EMPTY IT INTO THE PROPER WASTE CONTAINER. IF THE WASTE CONTAINER IS FULL, TAKE THE FULL BOTTLE TO THE DISPENSARY AND REPLACE IT WITH AN EMPTY ONE.

When you finish the analysis of your unknown and turn in your results, your TA may then discuss many of the chemical transformations that take place during these analyses. The nature of this experiment is such that a Chemistry 2C student can perform all the operations and arrive at an accurate analysis for an unknown without really needing to understand everything that is going on in the system chemically. In fact, you will probably appreciate the chemistry much better after you have finished all the experimental work and seen some things with your own eyes.