



Qualitative Analysis

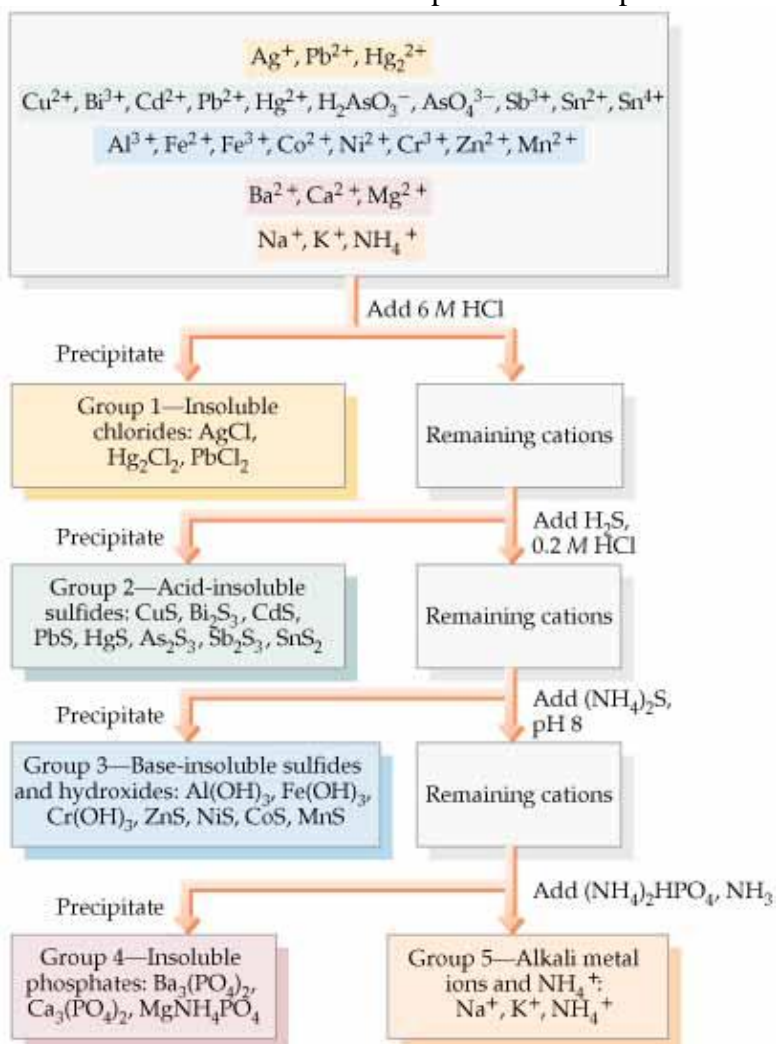
Experiment

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Introduction

Qualitative analysis is a method used for identification of ions or compounds in a sample. In many cases, qualitative analysis will also involve the separation of ions or compounds in a mixture. Examples of qualitative tests would include ion precipitation reactions (solubility tests) or chemical reactivity tests. The separation of ions is easily achieved by taking advantage of their solubility properties (Flow-Chart 1).

Flow-Chart 1. Cation Separation Example.



Quantitative analysis is a method used to determine exact amount. An example of a quantitative test would be an acid/base titration to determine concentration (volumetric analysis).

In this experiment, you will be required to identify the ions in an unknown mixture. You will work out your own scheme for analyzing a mixture containing some combination of a group of ions. There will be three unknowns for you to analyze based on three different groups of ions. They are as follows:

1. Cations (Group 1): Ba^{2+} , Ag^+ , Hg_2^{2+} , Cu^{2+} and Zn^{2+} . The unknown will contain no less than two, no more than four of the ions in this group.
2. Cations (Group 2): Ba^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Zn^{2+} and Al^{3+} . The unknown will contain no less than two ions in this group.
3. Anions (Group 3): Three groups of anions. In addition, you must look for and report H^+ , OH^- , NH_3 and NH_4^+ if present. There will be a maximum of six substances to report in this unknown.

For each set of samples, you will test a known set of standards to see how they react with certain reagents. Record your observations for each test in a table in your notebook. Your observations should include precipitation or no precipitation as well as colors. Then examine the results to decide how each of the ions could be identified when others are present. You may wish to test parts of your scheme on known combinations of ions.

Preparation of Reagents

1. Obtain a red plastic tray with six dropper bottles. If there are reagents in the bottles in your locker, empty them out and rinse the bottles with distilled water from your wash bottle.
3. Fill the dropper bottles with the solutions listed below. Follow these safety precautions.
 - a) These are very corrosive liquids. WEAR EYE PROTECTION when using them.
 - b) AVOID SPILLS by transferring the approximate volume wanted to a small beaker.
 - c) Label dropper bottles clearly and put your name and date on the reagent tray.

Reagents:	6M HCl	0.5M KOH
	6N=3M H_2SO_4	6M NaOH
	3N=1.5M H_2SO_4	6M NH_3 (labeled as NH_4OH)

The 15M NH_3 (concentrated) will be available in lab fume hood. Do not remove this bottle from the fume hood because it is fuming ammonia which will “stink-up” the lab.

Locker Equipment To Get In Order

1. Two test tube sizes will be used, 13 x 100 mm and 10 x 75 mm. To calibrate the test tubes, measure approximately 1 mL volume into each size tube so that you can estimate volumes easily.

Keep several capillary pipettes and rubber bulbs for them handy. Approximately 20 drops from these pipettes is equal to 1 mL.

2. Obtain or make a “puddler” (stirring rod). You should have a thin glass rod about 15 cm long and about 4 mm in diameter.

Lab Techniques To Learn

There are a number of procedures that you will do repeatedly. Refer to these notes as often as necessary to become familiar with them.

1. Neutralization. To test pH, use universal indicator paper unless otherwise directed. Tear each strip into several short pieces. Dip a glass rod or dropping pipette into the solution, and then touch it to the paper. Compare the color with the reference chart to estimate pH.

When adjusting pH, stir thoroughly after each addition of acid or base before re-testing with indicator paper.

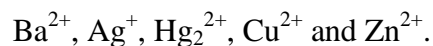
2. Isolating solids. Any solid formed by mixing solutions is referred to as a precipitate whether it settles out or not. The clear liquid portion of the solutions is called the supernatant liquid or the filtrate. Precipitates may be isolated by centrifugation.
 - a. Balance the test tube with one of the same size filled to an equal depth with water or solution. Place the two tubes at opposite ends of the centrifuge arm. Be sure the centrifuge cups are the right size for the tubes you are spinning. Close the lid. Turn on the switch to start spinning.
 - b. After spinning, switch off the motor and allow the centrifuge to come to a COMPLETE STOP before opening the lid and removing the sample and its counter balance. The knob on the lid is a brake. Push down on it to bring things to a final halt.
 - c. To isolate the solid, draw off the supernatant liquid with your capillary pipette.

Procedure

Part A (Day 1)

Preliminary Standards Tests

Cations group 1:



SAFETY NOTE: *The heavy metals are toxic. Therefore, wash your hands thoroughly with soap before leaving the lab. If the soap is not set out in the lab, ask your instructor for it. This hand washing should be a normal routine at the end of each laboratory period.*

The tests listed below should give you information about the behavior of these ions sufficient to work out a method of analysis. Record the data in ink directly in your lab notebook. It would be best to record the observations in a data table. Leave one column blank for your unknown tests

that you will run on day 2. Remember, your notes should show two things, what you did and what you saw. Conclusions can be drawn later.

For each of the following tests, take fresh 6-7 drops of each ion listed at the top of the page. Use the nitrate test solutions in the larger test tubes unless otherwise indicated. Add reagents drop wise with mixing until no further change is observed. Record your observations for the following six tests.

1. Test a few drops of each sample separately on your spot plate with KI.
2. Test a few drops of each sample separately on your spot plate with K_2CrO_4 . Don't mistake the color of the reagent for formation of a precipitate. Test the precipitates with HNO_3 to see if they dissolve on acidification.
3. Test each ion in a test tube with 1.5M H_2SO_4 .
4. Place 6-7 drops of each ion in a test tube and add 6-10 drops of 6M HCl.
 - a. Centrifuge tubes with precipitates, then test the filtrate with HCl to see if precipitation is complete. Isolate any solids that form and discard all filtrates.
 - b. Add about 12 drops 15M NH_3 to each of the solids from Step (a). Stir well and record observations.
5. In test tubes, test each ion with universal indicator paper, and then add enough 0.5M KOH to neutralize any solutions that are acidic.
 - a. Test each ion with 4-5 drops additional KOH past the neutralization point. Record observations.
 - b. Now add excess 6M NaOH (~ 20 drops) to each test tube and again record observations.
 - c. Centrifuge any precipitations and then add 1 drop of the NaOH ion solution (*supernatant* liquid) to a piece of the dithizone paper. A positive test for Zn^{2+} is the appearance of a bright pink spot, which spreads when a drop of water is added to it. Other ions and OH^- change the color of the paper, but note the difference in behavior.
6. Test each ion with 3-4 drops of 6M NH_3 . Record any changes. Then add excess 15M NH_3 drop wise with stirring. Again, record observations.

Evaluation Your Observations and Development of an Analysis Scheme

By the end of all of these tests you should be able to compare the way these ions behave toward each reagent, finding those with similarities and those with differences in each case. Check your observations against the reaction products listed at the end of this section. Repeat any tests that seem questionable. Organize your results into table.

Now you need to decide on a procedure to identify each of these ions if they are together in a mixture. The unknown will contain two to four ions and there will be about 7 to 8 ml to work with. Look for tests that will separate the ions from each other or allow you to identify one in

the presence of others. A flow-chart is helpful. Check through the notes below to make sure that your procedures will work for combinations of ions.

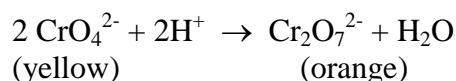
Notes on Analyzing Mixtures

1. When working with mixtures of ions there are some additional techniques that must be employed.
 - a. Take 12-15 drop samples when using them for separations.
 - b. For preliminary test on individual ions there is no need to wash precipitates. But for any procedure separating two or more ions, the precipitates must be washed as follows.
 1. Isolate the solid by centrifuging as you have done before.
 2. After lifting off the filtrate, wash the solid; add 1 ml water, stir and recentrifuge. Lift off the supernatant wash water, discard it and repeat the washing process with a second portion of water.
2. If you precipitate Hg_2^{2+} as the chloride (Test 3), then Ag^+ must be confirmed. After adding concentrated NH_3 to the chloride precipitates, add 6M HNO_3 drop wise to the NH_3 filtrate until it tests slightly acidic. If silver is present, AgCl will re-precipitate as soon as the NH_3 is neutralized. Test a known Ag^+ sample along with the unknown.
3. In carrying out a sequence of steps on the same sample, keep track of what has been previously added. Be aware of these cautions.
 - a. To precipitate hydroxides (Test 5), acids must be neutralized before the added base can begin to form a precipitate.
 - b. Soluble ammonia complexes (Test 4 and 6) can be decomposed by addition of acid ($\text{NH}_3 + \text{H}^+ = \text{NH}_4^+$). But the ammonia complex will form again if the solution is made basic ($\text{NH}_4^+ + \text{OH}^- = \text{NH}_3$). Therefore, Ag^+ , Cu^{2+} and Zn^{2+} will be soluble in any alkaline solution that has had NH_3 or NH_4^+ previously added.
 - c. The same principle applies to the dithizone test. Dithizone paper detects zinc only as $\text{Zn}(\text{OH})_4^{2-}$. This complex will not form in any solution containing NH_3 or NH_4^+ .
4. Chromate ion is converted to dichromate in acidic solution. Dichromates are generally more soluble than chromates. If you rely on K_2CrO_4 to confirm any ion, be sure to carry a known sample through the same procedure.

Reactions: Group 1 Preliminary Standards Tests

Along with the table summarizing the results of the tests, formulas of the precipitates should be given and balanced net ionic equations for the formation of soluble complex ions from precipitates.

- Test 1 and 2. Write the formulas of each solid with its characteristic color. I^- forms insoluble iodides with most of the ions. Note that some have very distinctive colors. CrO_4^{2-} gives colored precipitates. Remember that chromate ion changes color in acidic solutions (note 4 above):



- Test 3. H_2SO_4 precipitates only one ion, barium, as BaSO_4
- Test 4 (a) HCl precipitates the insoluble chlorides, AgCl and Hg_2Cl_2 . All can be solubilized by a large excess of chloride ions, so excessive quantities of HCl should be avoided. AgCl_2^- and $\text{Hg}_2\text{Cl}_4^{2-}$ are the colorless, soluble complexes formed
- Test 4 (b) Addition of 15M NH_3 to the silver and mercurous chlorides shows distinctive behavior for each:
- (1) $\text{AgCl} + 2\text{NH}_3 \rightarrow \text{Ag}(\text{NH}_3)_2^+ + \text{Cl}^-$
(soluble, colorless)
 AgCl dissolves, forming a soluble complex ion
 - (2) $\text{Hg}_2\text{Cl}_2 + 2\text{NH}_3 \rightarrow \text{HgO} + \text{HgNH}_2\text{Cl} + \text{NH}_4^+ + \text{Cl}^-$
(black) (white solid)
 Hg_2Cl_2 blackens due to formation of finely divided metallic mercury with simultaneous oxidation and reduction of the mercurous ion.
- Test 5 (a) KOH : small concentrations of hydroxide precipitate many of the ions as the hydroxides or oxides.
 Hg_2^{2+} disproportionates in this case also.
 $\text{Hg}_2^{2+} + 2\text{OH}^- \rightarrow \text{Hg}^0 + \text{HgO} + \text{H}_2\text{O}$ brown to black solid
 $\text{AgOH} \rightarrow \text{Ag}_2\text{O}$ brown $\text{Hg}(\text{OH})_2 \rightarrow \text{Hg}^0$ yellow
 $\text{Cu}(\text{OH})_2$ blue-white
 $\text{Zn}(\text{OH})_2$ white
- Test 5 (b) Excess NaOH causes the amphoteric hydroxides to dissolve.
 $\text{Zn}(\text{OH})_2 + 2\text{OH}^- \rightarrow \text{Zn}(\text{OH})_4^{2-}$
 Both ions form soluble, colorless complexes
- Test 6 6M NH_3 causes some ions to form soluble complexes.
 $\text{Ag}(\text{NH}_3)_2^+$ has already been observed in Test 3 (c).
 $\text{Zn}(\text{NH}_3)_4^{2+}$ is also colorless.
 15M NH_3 converts the blue-white $\text{Cu}(\text{OH})_2$ completely to deep blue $\text{Cu}(\text{NH}_3)_4^{2+}$.
 This intensely colored complex is distinctive for Cu^{2+} . (Is 6M NH_3 concentrated enough to do the conversion or must the 15M NH_3 be used?)

Part A (Day 2)

Obtain an unknown sample and repeat the above procedure for unknown group 1 ions. Record the unknown sample ID in your notebook.

Part B (Day 3)Preliminary Standards Test.

Group 2 ions:



The tests for this group of ions are much more definitive than those for the first unknown. Note that some solutions are saved for subsequent tests to save time and materials. As before, take 6-7 drops of each ion for testing. Set up a data table for the standards and the unknown.

1. a. Test each ion with a few drops of 6M NaOH, then add excess. Save the filtrates of all six ions for test 6. Discard precipitates.

b. Test a drop of each of the clear solutions on dithizone paper and record the results.
2. Test each ion with a few drops 15M NH_3 . Stir thoroughly, then add an excess, stirring again. Save filtrates of all six ions for test 7. Discard precipitates.
3. Test each ion with 3M H_2SO_4 .
4. Test all the ions with 3M NH_4SCN . Add a little solid NaF to any solution that changes color. Any solid in the tube is excess undissolved NaF, not a precipitate. Observe the colors and then add NaSCN-saturated acetone.
5. Check the pH of each ion, then test with K_2CrO_4 on a spot plate. Record observations. Then acidify solutions slightly with 6M HCl and note any changes.
6. a. Neutralize all six filtrates from test 1 with 6M acetic acid, checked with universal indicator paper. Then add 6M NH_3 to make barely alkaline. Aluminum should give a white precipitate. Centrifuge all tubes containing a precipitate. Discard the clear supernatant and save the precipitates for the next step.

b. Add $\frac{1}{2}$ ml 6M ammonium acetate to the precipitate. Then add acetic acid or NH_3 dropwise as needed to adjust the pH between 5 and 7, tested with narrow range pH paper available from the instructor. Dribble 5 or 6 drops of aluminon reagent down the side of the test tube. A red lake should develop within a few minutes. A lake is the term used when a dye is absorbed onto the surface of a solid, in this case $\text{Al}(\text{OH})_3$. A positive test for aluminum should show color from the aluminon reagent removed from the solution and absorbed onto the solid, forming intensely colored pink beads. The color lasts several days.
7. Add 6 drops of 1% dimethylglyoxime solution to each sample saved from Test 2. To be reproducible, this test must be performed on a solution containing ammonia.

Do any of these ions form sulfate or chloride precipitates? Notice that some ions form soluble ammonia complexes analogous to those observed for silver and copper. Some are *amphoteric*, precipitating as hydroxides or oxides in dilute base but forming soluble hydroxy complex ions in more concentrated base. Go over your tests to decide how you can identify each of these ions in the presence of any other.

Part B (Day 4)

Repeat the above procedure for unknown group 2. Your tests should show conclusively whether each of the six ions is present or absent. Record your sample ID number in your notebook.

Part C (Day 5)Preliminary Standards Tests

There are four groups of anions. They are:

Group A: Cl^- , Br^- or I^-

Group B: SO_4^{2-} , CO_3^{2-}

Group C: PO_4^{3-} or CrO_4^{2-}

No more than one anion will be present from any group. For example, if the unknown has Cl^- , it will not have Br^- or I^- .

In addition, you must test for Group D: H^+ , OH^-

Group E: NH_3 and NH_4^+

Follow the procedures given below to test known ions selected from any of the solutions available on the reagent shelf in your locker reagent tray. These anions are just the counter ions to the cations in each reagent. For the acid and base tests, you can just use HCl and NaOH. For the ammonia test use ammonium hydroxide and for the ammonium test use ammonium chloride.

Preliminary Tests:

Group A. Cl^- , Br^- , I^- Make the silver salt of the three ions by adding AgNO_3 to an acidic portion of each sample. Isolate any precipitate. When testing for an unknown for halides, be sure that solution is strongly acidic by adding 6-8 drops 6M HNO_3 to the test solution before adding the AgNO_3 . Many other anions precipitate with Ag^+ if the solution is not acidic enough. To be sure, test the known ions including carbonate, chromate and phosphate along with your known.

AgCl is soluble in 6M NH_3 as you have already learned. AgBr and AgI are insoluble. If you have a precipitate that is not AgCl , the following test will identify iodide and bromide.

Iodide test.

Acidify a sample of the iodide anion with acetic acid. Add a few crystals of solid KNO_2 . Appearance of a brownish (or lavender?) color indicates the formation of I_2 . Add 1 or 2 ml mineral oil with vigorous stirring. I_2 will appear purple in the oily layer. Br^- will not react. Dispose of the mixture in the hood drain.

Iodide and bromide test.

To identify and confirm bromide or iodide add 10 drops of 3% NaOCl solution to a fresh sample of the standard. Add 10 to 15 drops of mineral oil and mix vigorously. OCl^- will oxidize both these halides and they will show distinctive colors when extracted into the mineral oil layer.

Group B and C. These ions all form solids with Ba^{2+} . Take 10 drops of your standard and make sure it is slightly basic, then add $\text{Ba}(\text{NO}_3)_2$. Isolate any solid. Acidify the solid by adding HCl . Then continue with the following tests.

Group B. SO_4^{2-} , CO_3^{2-} Both sulfate and carbonate precipitate with Ba^{2+} . BaSO_4 is insoluble in acid. BaCO_3 dissolves when acidified with evolution of bubbles of CO_2 gas.

Group C. CrO_4^{2-} , PO_4^{3-} These also form solids with Ba^{2+} , however, both solids dissolve in HCl without evolution of a gas. This additional test may be necessary. Add 6M NH_3 to the HCl filtrate until the solution tests slightly basic. Phosphate and chromate should both re-precipitate as the barium salts.

Group D. H^+ and OH^- . You should need no help in testing for these ions.

Group E. NH_3 and NH_4^+ . Place 10 to 20 drops of your standard sample in a casserole and make the solution alkaline with NaOH . Gently heat almost to boiling and test the vapors with moist red litmus. If NH_3 is present, the paper will turn blue. Do not mistake splatters of the basic solution of the litmus for a positive test. If ammonia is present, you must decide whether it was originally present in the unknown as NH_3 or NH_4^+ .

Part C – (Day 6)

Repeat the above procedure for unknown 3 anions. No more than one anion will be present from any group. For example, if the unknown has Cl^- , it will not have Br^- or I^- . Record your unknown ID number in your notebook.

Data Analysis

Tabulate all data.

Identify the Ions in each of the unknowns (make sure unknown ID number is clearly displayed).

Discuss any complications with the tests results. Did any give mixed result?

No report is needed for this experiment. Turn in your flow-charts and data tables with the results.