Chemistry 201

Qualitative Analysis

Introduction

General comments: It is always a good idea to use as few chemicals as possible; it makes sense both from consideration of lab safety and chemical waste disposal. Therefore, keep in mind that each of the chemical tests that are discussed below can be done with a few drops of solution. Remember that when using such small amounts, it is extremely important that the equipment that you use is very clean. If the equipment is "dirty," the solutions will become contaminated, and it is possible that you will identify the contaminant rather than the unknown. To avoid cross contamination, make sure to recap reagent bottles with the original caps and to clean your droppers very well if they are to be reused.

Color of solution: The color of a solution can provide a clue to its chemical contents. Of the ions commonly encountered in this course, aqueous solutions of transition metal cations will often be colored since the valence d-electron energy levels of transition metal complexes can often absorb light in the visible region of the spectrum. This absorption of visible light causes the solutions to appear colored (see Figs. 23.5 and 23.6 in Silberberg). In contrast, cations of alkali (group 1A), alkaline earth (group 2A) metals and ammonium ions are colorless since the electrons of these ions do not absorb light in the visible region of the spectrum. A table of the colors of a selection of cations in aqueous solutions is given in the margin note area. The color of a solution is a simple type of absorption spectroscopy.

Ion	Solution Color
Li^+, K^+, Na^+, Ba^{2+}, Ca^{2+}, NH_4^+	Colorless
Fe^{3+}	Yellow
Ni^{2+}	Green
Cu^{2+}	Blue

Flame test: The flame test is used in qualitative analysis to identify ions such as sodium, barium, potassium, calcium and others. In this test, the sample is vaporized in a flame and the flame becomes brightly colored as a result of light emitted from atoms and ions in excited energy states. In many cases, the color of the observed flame can be correlated to the chemical identity of the cations and anions in the solution (see Fig. B7.1, in Silberberg). A table of several such correlations is given in the margin note area. The flame test is a simple type of emission spectroscopy.

Ion	Flame Color
Li^+	Red
Na^+	Yellow
K^+	Violet
Ca^{2+}	Dark Red
Cu^{2+}	Green
Cl^-	Faint Green
Ba^{2+}	Green

The flame test is fast and easy but requires some practice to reliably produce and see the colors (some ions will be more intensely colored than others). To carry out a flame test, you will use a clean inert wire and a clean watch-glass with a few drops of the aqueous solution. Clean a piece of nichrome wire (or paper clip) by first heating the wire in a hot Bunsen burner flame until it glows red hot. Dip the wire into a nitric acid (or hydrochloric acid) solution (see safety note in margin area), heat again, and then rinse with distilled water. Repeat these steps until the wire burns without color. To test an unknown, place some unknown solution onto a watch glass and hold it next to the air inlet at the bottom of your Bunsen burner. Heat the wire in the flame and then plunge the hot wire into the solution in the watch glass. This will vaporize the solution, allowing it to be carried with the air into the flame producing a colored flame. If you have any questions regarding the test, ask your professor to demonstrate.

Solubility: Many qualitative analysis schemes have been proposed that rely on the selective precipitation of specific cations and anions based on their solubilities. When two solutions are mixed, a compound formed from a cation in one solution and an anion in the second solution will precipitate if its concentration is higher than its solubility (see Section 4.4 of Silberberg). Therefore, the solubility test can be conducted by mixing a few drops from two different solutions and noting whether a precipitate forms. (The formation of a solid precipitate will be evident due to the increased turbidity of the mixture).

For qualitative analysis, often only general trends in solubility need to be known. These trends can be summarized by a set of relatively simple rules, often referred to as "the solubility rules" and are given below. Also see table 4.1 of Silberberg.
(**Solubility is defined as greater than 0.01 mol/L at 25° C**)

ANION	+	CATION	COMPOUND THAT IS:
Any	+	Alkali metal ions, or NH_4^+	Soluble
NO_3^-, ClO_4^-	+	Any	Soluble
Cl^-, Br^-, I^-	+	Any, except Ag^+, Pb^{2+}, Hg_2^{2+}, Cu^+	Soluble
SO_4^{2-}	+	Any, except Sr^{2+}, Ba^2, Pb^{2+}.	Soluble
OH^- ,S^{2-}	+	Any, except alkali metal ions, NH_4^+, Sr^{2+}. , Ca^{2+} , Ba^{2+}	Insoluble
PO_4^{3-}, CO_3^{2-}, SO_3^{2-}	+	Any, except alkali metal ions, NH_4^+	Insoluble

Acidity: The pH test is used to determine the acidity of aqueous solutions. By placing a drop of a solution on pH indicator paper, the pH can roughly be determined. The color of the indicator paper after it is wetted with the test solution is correlated to pH (see text box in margin note area).

For qualitative analysis, it is useful to divide the pH scale into at least three categories: strongly acidic (pH<3), neutral (pH~7), and strongly basic (pH>10). Sometime the two additional categories, weakly acidic (3<pH<6) and weakly basic (8<pH<10), are also used.

When a substance dissolves in water and causes an increase in the concentration of protons (H^+), the substance is considered to be an acid. For classification purposes, we will define solutions with ***pH < 3 as strongly acidic***. Examples of strong acids that you may encounter this semester include: HCl, H_2SO_4, HNO_3 or H_3PO_4.

For the type of pH paper you will use:

- Red ⇨Acidic
- Orange⇨Neutral
- Blue ⇨Basic

Aqueous solutions of some metal ions also test acidic. The acidity is due to complexes that form between the metal ions and water. For instance, a 0.25 M aqueous solution of Fe^{3+} will test strongly acidic. This is due to the following equilibrium,

$$Fe^{3+}(aq) + 6H_2O(aq) \leftrightarrows [Fe(H_2O)_6]^{3+}(aq) \leftrightarrows H^+(aq) + [Fe(H_2O)_5OH]^{2+}(aq)$$

Other metal ions (such as Pb^{2+}, Cu^{2+}, Al^{3+} and Zn^{2+}) will test only weakly acidic (3<pH<6).

When a substance dissolves in water and causes an increase in the concentration of hydroxide ions (OH^-), the substance is considered to be a base. For classification purposes, we will define solutions ***with pH > 11 as strongly basic***. Solutions with pH > 11 result from the presence of OH^-, NH_3, CO_3^{2-}, or PO_4^{3-}.

Cations and anions that do not tend to form excess protons (H^+) or hydroxide ions (OH^-) will test ***neutral*** (pH≈7). Solutions of salts formed by cations of groups 1A and 2A (such as Na^+, K^+, Ca^{2+}, and Ba^{2+}) and anions of strong acids (such as Cl^-, SO_4^{2-} SCN^-, and NO_3^-) will be very close to pH≈7. Remember, the stronger the conjugate acid, the weaker the conjugate base. For example, since hydrochloric acid is a very strong acid, the conjugate base, Cl^-, has virtually no tendency to gain a proton. Additional information about acid-base chemistry can be found in Silberberg, sections 4.4 and chapter 16.

Gas-Producing Reactions: Some reactions form gaseous products that can easily be detected by observing bubble formation. For example, perhaps you have had the experience of adding vinegar (CH_3COOH) to baking soda ($NaHCO_3$). This is an example of a gas-forming reaction. The resulting chemical reaction can written as,

> **Safety Note**: When a gas is expected to be produced, make sure to point the reaction test tube away from all people, in case the reaction mixture shoots out of the tube.

$$CH_3COOH\ (aq)\ +\ NaHCO_3\ (s) \leftrightarrows CO_2\ (g)\ +\ H_2O\ (l) + CH_3COONa\ (aq)$$

or alternately the reaction can be written in net ionic form as,

$$HCO_3^-\ (aq)\ +\ H^+\ (aq) \leftrightarrows CO_2\ (g)\ +\ H_2O\ (l)$$

In addition to being a gas-forming reaction, you should recognize that this reaction is also an example of acid-base chemistry. Predictably, this type of reactivity can be extended to the base, carbonate (CO_3^{2-}), which can react with an acidic solution causing the formation of carbon dioxide bubbles due to the following reactions,

$$CO_3^{2-}\ (aq) + 2H^+\ (aq) \leftrightarrows HCO_3^-\ (aq)\ +\ H^+\ (aq) \leftrightarrows CO_2(g) + H_2O(l).$$

A smelly example of a gas-producing reaction is an aqueous ammonia (also known as ammonium hydroxide) solution. Ammonia (with its characteristic odor) can be released by the equilibrium between a solution of ammonium hydroxide (solublized ammonia) and ammonia gas.

> **Safety Note**: If you decide to smell the odor of a chemical, minimize your exposure to chemicals by smelling as small of an amount as possible. Wave the chemicals towards your nose, rather than directly smelling the container.

$$NH_4^+\ (aq)\ +\ OH^-\ (aq) \leftrightarrows NH_3\ (g)\ +\ H_2O\ (l).$$

Complex ion formation: Many transition metals ions are known to form colored complexes when bonded with specific molecules or anions in an aqueous solution. Therefore, the color change observed when an unknown solution is added to a known metal ion containing solution can be applied in qualitative analysis schemes.

Consider as an example, what happens when aqueous ammonia (also known as ammonium hydroxide) is added to a solution containing copper (II) cation, which is initially light blue-green. Since ammonium hydroxide (NH_4OH) solutions are basic, when a small amount of aqueous ammonia is added to a Cu^{2+} solution, a light blue precipitate of $Cu(OH)_2(s)$ is formed according to the reaction,

$$Cu^{2+}(aq) + 2OH^{-}(aq) \leftrightarrows Cu(OH)_2(s),$$

However if you continue to add ammonium hydroxide to the $Cu(OH)_2(s)$, a second type of reaction take place. A complex ion reaction produce a deep blue solution of the soluble copper complex $[Cu(NH_3)_4]^{+2}(aq)$,

$$Cu(OH)_2(s) + 4\,NH_4^{+}(aq) \leftrightarrows [Cu(NH_3)_4]^{+2}(aq) + 2H^{+}(aq) + H_2O(l)\ ,$$

The complex ion, $[Cu(NH_3)_4]^{+2}$, can also be formed directly by the addition of excess ammonia to an aqueous solution of $Cu^{+2}(aq)$. Similarly, aqueous Ni^{2+} ions (green) can bind ammonia to form a purple complex of $[Ni(NH_3)_6]^{+2}$.

Another colorful example of complex ion formation is the ferric thiocyanate complex. When a yellow, iron(III) solution is mixed with a colorless thiocyanate (SCN^{-}) solution the blood red ferric thiocyanate complex is formed.

$$Fe^{3+}(aq) + SCN^{-}(aq) \leftrightarrows [FeSCN]^{2+}(aq), \text{ or more accurately,}$$

$$Fe^{3+}(aq) + 5H_2O(l) + SCN^{-}(aq) \leftrightarrows [Fe(H_2O)_5\,SCN]^{2+}(aq).$$

Case Study Activity

A. The Challenge:

Welcome. You are now a member of a special investigation team. Because of your academic strength and problem-solving skills, you and your team have been selected to help us clean up the laboratories. It seems that last semester's chemistry class wasn't very careful. When we were cleaning up the labs earlier this month, we found five bottles of unlabeled chemical waste. To dispose of these bottles, the chemicals in each bottle will have to be identified. (It would be both illegal and unethical to dispose of unknown chemicals by putting them down the drain or in a trash container.)

Preparation

- Review basic chemical reactions.
- Read this lab
- Review Silberberg Chapters 1-4.

Since we know the types of experiments that were carried out the previous semester, we know that the bottles contain the following chemicals: barium nitrate [$Ba(NO_3)_2$], nickel(II) chloride [$NiCl_2$], ammonium hydroxide (NH_4OH), sodium carbonate (Na_2CO_3), and sulfuric acid (H_2SO_4). Further, it seems fairly unlikely that a single bottle would contain a mixture of the possible chemical components.

It is now your responsibility to identify the contents of these bottles. The only tools you have available are the chemical unknowns themselves, pH paper, a Bunsen burner, disposable pipets, paper clips, empty beakers, glass stirring rods, a bottle of rinse water, and your knowledge of chemistry.

B. Preparing for the challenge:

One important skill that you will need to develop this semester is the ability to collect and organize scientific information. Since you will often be asked to do this as you go along, it will be to your advantage to plan ahead. This preparation should be done in your laboratory notebook. Your laboratory notebook is your permanent record of your entire laboratory experience, from the preparation stage to the end of the laboratory experiment. Everything you do for case study and laboratory **should be recorded in your laboratory notebook in ink.** Copies of your case study and laboratory work will always be collected **at the end of the period** and your pre-laboratory exercises will always be collected at the start of each laboratory session; all items will be graded.

Even before case study, you should begin to **evaluate** the problem that you will face. For example, for the case study at hands, you should skim Chapters 1-4 of you textbook (Silberberg) and read the introduction of this experiment in order to be familiar with the relevant chemical information that you will use to solve the chemical challenge.

By the end of this evaluation phase of the problem, you should be able to succinctly state the problem and to be aware of the types of chemical knowledge that you will need to bring to bear. Don't be surprised if you are called on in case study and asked to verbally highlight some of the background chemistry needed to solve the problem. It would be useful for you to organize your thoughts by providing summaries of the possible chemical compounds and the types of chemical tests that will be used.

As the second step of problem solving, you will want to start to **examine** specific observations and begin to correlate these observations to chemical ideas in order to define an experimental strategy. Most of the time you will need to wait until case study to begin this step, so be ready to think on your feet. In case study, when we make observations as a group, you will need to record those observations in some kind of organized format.

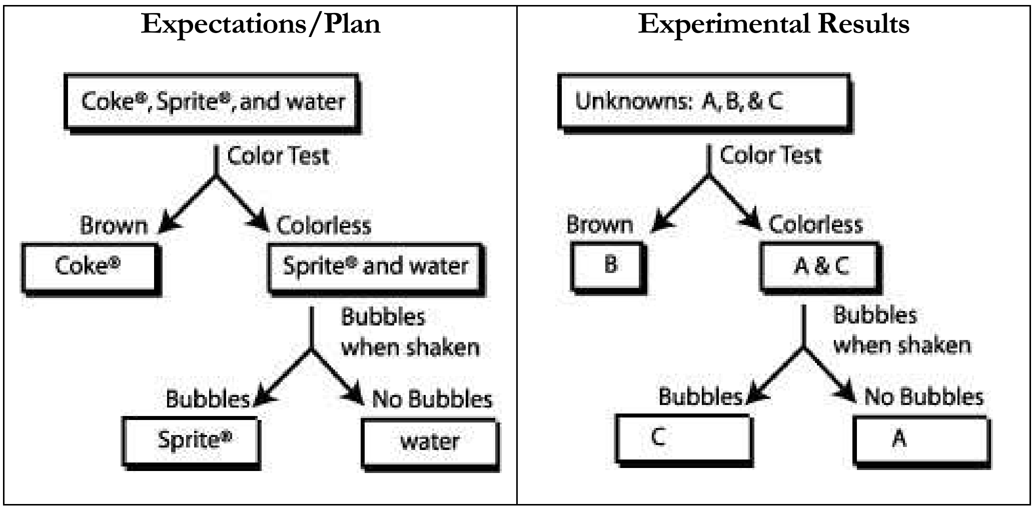
Chemical Component
1. Barium nitrate [$Ba(NO_3)_2$],
2. Nickel chloride [$NiCl_2$]
3. Ammonium hydroxide (NH_4OH),
4. Sodium carbonate, Na_2CO_3
5. Sulfuric acid, (H_2SO_4)

Chemical Tests
1. Color of solution
2. Color of flame
3. Acid-Base reactivity
4. Precipitation reactions
5. Complex ion reactions
6. Gas producing reactions

For example, when you get to case study and examine the unknowns, you might use a table similar to the one below to summarize your initial observations.

Bottle label	**Observation**
Unknown 1	Approximately 25 mL of a clear, colorless, odorless liquid.
Unknown 2	Approximately 25 mL of a clear, yellow, odorless liquid.

So do you think you are ready? …. Here is one last thing to think about. In the case of qualitative analysis, it is often useful to outline the problem using flow charts. These charts are useful both in communicating the procedure that was followed, as well as the logic that was used in carrying out the analysis. As a quick example, consider the problem of identifying three cups; one of Coke®, one of Sprite®, and one of water. The flow diagrams for such a problem might look like the following:



Note that each vertical line represents a test, and that each distinct result is grouped in its own box. In this way, the application of successive tests can be expected to separate the unknowns according to their characteristic properties. By correlating the properties of the unknowns to the properties of known samples, the identities can be realized.

C. The Case Study Session

In case study, we will be working together to identify five bottles of unknowns. As we work through this problem, you will want to record the experimental strategy used (e.g. in a flow diagram), any observations that you make (e.g. in summary tables), and any conclusions that you are able to draw (e.g. in summary statements). Although you will need to present this information in your own style, the instructor will be acting as your guide throughout the activity. If at any point you have a question, be sure to ask!

During the case study you will want to make sure to take notes. In particular, the things that we will be looking for in scoring the work that you turn in include:

1. Your name and section number.

2. A list of the tests that you would like to run first during the investigation.

3. A flow chart of your expected results.

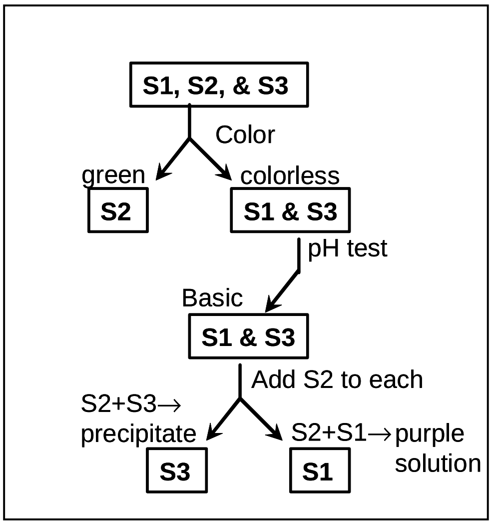
4. A flow chart of the observed results.

5. A table summarizing the conclusions.

IV. Pre-Laboratory Activity

1. Safety is very important in the chemistry lab. It is a good laboratory practice to always be familiar with the hazards of the chemicals that you will be handling. Therefore, please read the pertinent information on all of the chemicals that are used in the experiment by looking up the Material Safety Data Sheet (MSDS) for each chemical before you arrive to lab. This can be done quickly and efficiently by going to http://ccc.blackboard.com and logging into the course Blackboard. The experiment link will present a summary of table of chemical safety information and will facilitate accessing the MSDS information for the chemicals used in this experiment. Please record the names of all the chemicals that have a health hazard rating of 3 or above.

2. Suppose you are given three bottles, labeled S1, S2, & S3, each contains an aqueous solution. You are told that the possible solutions are: **Nickel (II) sulfate, sodium carbonate, ammonium hydroxide (6. *M*), potassium thiocyanate, and pure water**. Only one type of solution is present in each bottle and the concentration is 0.5 *M* unless otherwise noted. Several tests are run, and the results are summarized in the flow chart displayed on the right. Based on these results, assign the contents of the bottles and write a brief justification for each assignment.



3. To prepare for laboratory:

A. Prepare a table to summarize your initial expectations for the pH and color test. For each of the eight unknowns solutions that you will identify in lab, identify the pH category (acidic, neutral, or basic) and the color that you expect to find.

B. Although in your laboratory section you will be free to choose the order of the chemical tests that you carry out, for this pre-lab suppose that you planned to run the **pH test first** and the **color test second**. Create a flow chart that presents your expected results for the eight unknowns that you summarized in the question (3A) above.

C. Finally, write a balanced, net ionic reaction for the reaction of aqueous solutions iron (III) nitrate (also called ferric nitrate) and sodium phosphate. (Hint: remember to include the physical state: s, l, g, or aq.)

Lab Chemicals
Sulfuric acid, barium nitrate, sodium bicarbonate, potassium thiocyanate, sodium hydroxide, ferric nitrate, ammonium hydroxide, copper nitrate. Solutions will be delivered as aqueous unknowns in numbered dropper bottles. A concentrated acid solution will also be available for cleaning flame test wires.

V. Laboratory Activity

A. Introduction- Fictitious Scenario

The Chem-Police, a division has just discovered eight bottles containing solutions of potentially hazardous chemicals in Truman's Parking Garage. Your job to identify the chemicals and have the site cleaned up and ready to go before the employees start showing up in the morning.

The bottles are found to be labeled with a numerical code, and the math department code breakers are working on the code, but a chemical solution to this problem seems more direct. As part of the challenge, the group suggests that each bottle contains only one of the eight solutions listed below. Attached to each bottle there is one poorly written poem which obviously written by a chemist gone mad.

The concentrations are all 0.25 M unless specified otherwise. It is the task of your team to identify the contents of each bottle. This job must be completed in the field since the bottles cannot be transported from their original location until you identify their contents. In the field, you will only have pH paper, a Bunsen burner, paper clips wire (and concentrated acid solution for cleaning the wire), test tubes, droppers and spot plates. No other chemicals are available.

H_2SO_4(1M)	Formed with cation of acid fame, if precipitates anion and element 56 to blame.
$Ba(NO_3)_2$	March 17th has a color they say, that is the same as this chemical's flame test display.
$NaHCO_3$ (10%)	Not as basic as you might think, but adding an acid might help establish a link.
KSCN	A bloody mess you might see if you put this together with iron (III).
NaOH	BASICally you will find, this one's easy if you use your mind.
$Fe(NO_3)_3$	Roses are red and violets are blue, red with litmus and thiocyanate too.
NH_4OH (6 M) (aqueous NH_3)	Very emotional and complex, with copper quite blue, too strong to hold close, causes many to say "PEW!"
$Cu(NO_3)_2$	Color is the key and is easy to see.

B. Your Laboratory Challenge

Part 1 Group Unknowns (Teams of 2-3):

A set of the eight possible unknowns, labeled with identification numbers, will be available at your lab bench. Your lab team will determine the identity of each of the unknowns and will report the results as a group.

Safety Note: In this lab be careful of strong acids, strong ammonia odor. Be sure you know how to safely handle each chemical.

Each member of the team should be prepared. As part the pre-lab preparation, each member should have **evaluated** the problem so that he/she is familiar with the background information and the experimental objectives. Therefore, the first task to be accomplished by the group is to **explore** the problem: brainstorm to formulate an experimental strategy, perhaps carry out a few quick experiments, and distribute the work so that everyone knows what to do. It is important for each team member to make a definable contribution to the overall project.

While you **execute** your plan, using the chemical methods described in Section II- Chemical Foundations, it is important that you record your results. You should have already read ahead to the section on Communicating Your Results and know that you will be required to present your work in a flow diagram. Therefore, you will probably want to make this diagram as you collect your data. Remember to compare notes and run checks as needed. Every member of the team is responsible for knowing what the team did, what results were obtained, and what conclusions were drawn from those results.

Once you are confident of the group's conclusions, summarize the group's results and report the results to your teaching assistant. After the group's results have been reported, each member of the team will be given an individual unknown to identify.

Part 2 Individual Unknown (Individually):

When you obtain your individual unknown, you should immediately record the unknown number in your laboratory notebook. Since there are NO refills on individual unknowns, you should also make sure that you have at least 2 mL of unknown solution (the vial should be more than half full).

All of the work in this second part of the experiment should be done as an individual. Do not discuss your strategy or results with other members of your laboratory section. Teaching assistants can deduct points for inappropriate discussion during this second part of the laboratory challenge. However, you can use any of the previously identified solutions and any notes that were taken during the first part of the experiment.

Waste: Dispose of your waste in labeled chemical waste bottle located in the fume hood or according to the specific instructions of the professor.

Safety Note:
Do not put chemicals down the drain. Collect your waste at your laboratory bench and dispose of waste in the labeled chemical waste collection bottles located in the fume hood in lab.

C. Communicating Your Results

Group results can be worked on as a group and a single copy turned in for a grade (make sure to include the names of all group members). It is extremely important that every member of the group should agree with what is submitted. Every member must have his/her own record of the data and results recorded in his/her own notebook. The group report should include:

1. A **flow chart** illustrating the experimental strategy and experimental results. This diagram can be supplemented by other observations. All observations should be presented in an organized way.

2. A **table** summarizing the group's results. This summary should include the serial numbers of the unknowns and a brief written statement for each unknown explaining how an unambiguous conclusion was reached. The reasoning should be based on the tests run and should have a chemical basis for the result (not only process of elimination). *For example: sample A12345 was determined to be Nickel Sulfate because* Ni^{2+} *ion is the only ion amongst the given chemical set that would be expected to show a green color in aqueous solution and A12345 was green.*

<u>Working as an individual</u>, report the following in your laboratory report.

3. Select four reactions that were carried out during the laboratory period (either during the group work or while working on the individual unknown); one reaction should be selected in each of the following four categories: (a) acid base reactions, (b) complex ion reactions, (c) gas forming reactions and (d) precipitation reactions. For each reaction write a balanced chemical reaction including physical states [solid (s), liquid (l), gas (g) or aqueous solution (aq)]. Net ionic reaction equations are preferred, but not required. For example, the reaction of nickel(II) chloride and ammonium hydroxide seen in case study could be written in either of the following ways:

   $NiCl_2$ (aq) + 6 NH_4OH (aq) → $[Ni(NH_3)_6]Cl_2$ (aq) + 6 H_2O (l) or

   Ni^{2+} (aq) + 6 NH_4^+ (aq) → $[Ni(NH_3)_6]^{2+}$ (aq) + 6 H^+ (aq).

4. Attach a flow chart showing the procedure you worked out to determine your individual unknown and write a summary statement briefly explaining how you deduced the identity of your individual unknown.

Note: It will save time if you work on the report items while you are doing the experiment rather than waiting until the end of the period.

Group Unknown Identity Report Form

Group member Names: ________________________, ________________________,

________________________.

Initial Results: Based on our experimental results we have assigned the following identities to our unknown samples and are submitting the results to be graded.

Chemical Name	Unknown Number	Chemical Name	Unknown Number
Ammonium Hydroxide		Potassium Thiocyanate	
Barium Nitrate		Sodium Bicarbonate	
Copper(II) Nitrate		Sodium Hydroxide	
Iron(III) Nitrate		Sulfuric Acid	

NUMBER CORRECT: ________

Final Flow Chart of Experimental Procedure Used:

Individual Unknown Number:

↓ Tests:____________

Chemical Name	Written justification for assignment (Tests Ran)
Ammonium Hydroxide #________________	
Barium Nitrate #________________	
Copper(II) Nitrate #________________	
Iron(III) Nitrate #________________	
Potassium Thiocyanate #________________	
Sodium Bicarbonate #________________	
Sodium Hydroxide #________________	
Sulfuric Acid #________________	

References

1. **University of Iowa, Chemistry 004:011 Lab Manual, 2002**

2. **http://www.wiredchemist.com/chemistry/instructional/chem_lab_qualitative.html**

3. **Virtual CrezLab, http://www.crescent.edu.sg/crezlab/Webpages/PrelimExam4.htm**

4. **http://www.gk12.ilstu.edu/chemistry/PowerPoint202006/LABS%20&%20Activities/Qualitative%20Analysis/Introduction%20to%20Qualitative%20Analysis.doc**

5. **http://www.dartmouth.edu/~chemlab/chem3-5/qual_an/full_text/intro.html**