INTRODUCTION TO QUALITATIVE ANALYSIS

The primary duty of some chemists is to analyze substances for composition. So far in the chemistry course sequence only minimal consideration has been given to analytical techniques, and those considerations have been quite random.

The experiments in this section intend to give you an introduction to analytical procedures, principles and equipment. They illustrate the type of thinking that must take place to be a successful analyst. The experiments are in no way a thorough treatment of the whole subject. That kind of treatment is unending and even for the most causal chemist would certainly extend beyond this course. These experiments are just the staring place.

Chemical analyses are generally divided into two broad categories, qualitative analysis and quantitative analysis. Qualitative analysis deals with the determination of what is present. The experiments in this section address this interest. Quantitative analysis deals with the determination of how much is present.

The analysis of a substance can be a very difficult task. Given the fact that there are thousands and thousands of combinations, the possibilities must be narrowed down to have any reasonable expectation of success. Chemical substances are generally divided into two large groups, inorganic and organic. We begin our study of qualitative analysis by considering only inorganic substances. Organic compounds are dealt with in a later course. This immediately narrows the possibilities to less than half. To further narrow them down, we will consider a few, nowhere near all, of the more common inorganic substances. The substances chosen are those compounds formed when certain metallic cations (+ ions) and non metallic anions (- ions) combine. The ions selected are shown in Table 1, on the next page. These few ions, by combining with each other, can generate several hundred compounds. Notice how the cations are listed in groups. This is because of the procedures used to isolate and identify them.

It would be ideal if there were single simple tests that could be applied for the identification of each individual ion in the presence of other ions. Such tests are rare. To illustrate, if a solution contains silver ion, a white precipitate will form when $HC1$ is added to that solution. Ag^+ and $C1^-$ react to form insoluble $AgC1$, the white precipitate. It would seem that a good way to detect silver in a compound would be to dissolve some of that compound in water, add $HC1$, and look for a white precipitate. The only thing wrong with the scheme is that other ions behave in a similar manner. The other ions are Hg_2^{2+}, and Pb^{2+}. If a solution is prepared that contains a number of different ions and $HC1$ is added, the formation of white precipitate indicates the presence of Ag^+, Hg_2^{2+}, Pb^{2+}, or any combination of the three with no obvious way to tell. The white precipitate can however be separated from the original solution, then tested further to determine which of the three ions are present. The fact that Ag^+, Hg_2^{2+}, and Pb^{2+} are collectively separated from a mixture of ions by $HC1$ places them in analytical Group I.

There are five analytical groups of the cations as shown in Table 1. Also shown in the table are the precipitating agents for each group. The properties of the groups and individual ions that compose them will be studied in Experiment 15.

Anions tend **not** to group themselves as well as cations so we rely more for their identification on individual tests called "elimination" and "conformation" tests. These tests will be studied in Experiment 15.

The total process of separating and identifying ions is qualitative analysis. As you work your way through experiment 15, your knowledge of qualitative analysis will gradually increase to include all the ions listed in Table 1, and hence the compounds they can combine to form.

Table 1 – Common Inorganic Ions

Cations (Grouped)

Group No.	**I**	**II**	**III**	**IV**	**V**
Precipitation Agent	$C1^-$	S^{2-} low pH	S^{2-} high pH	CO_3^{2-}	None
	Ag^+	Bi^{3+}	CO^{2+}	Ba^{2+}	Cs^+
	Hg_2^{2+}	Cd^{2+}	Cr^{3+}	Ca^{2+}	K^+
	Pb^{2+}	Cu^{2+}	Fe^{2+}	Sr^{2+}	Mg^{2+}
		Sn^{2+}	Fe^{3+}		Na^+
		Sn^{4+}	Ni^{2+}		

Anions (Alphabetical)

Br^-
CO_3^{2-}
$C1^-$
$C_2O_4^{2-}$
I^-
NO_2^-
NO_3^-
PO_4^{3-}
SO_3^{2-}
SO_4^{2-}

A. **Procedures:** There are a number of experimental techniques commonly used in all qualitative analyses. They will be referred to without explanation as part of the procedure of the experiments. A discussion of the procedures follows and time spent learning about them now will be well worth it in terms of time saved in the lab and improved experimental results.

1. **Clean Equipment:** Clean glassware especially is essential for good results. Many of the tests used are quite sensitive and would be able to detect the presence of impurities that might come from unclean containers. Use the available detergents and brushes to thoroughly scrub the equipment. Make a final rinse of the equipment with distilled

or de-ionized water before using. Regular tap water contains unwanted ions.

2. **Reagent Bottles:** As a part of the locker equipment, there is a set of small dropper bottles in a wooden rack. Use these bottles to develop a convenient supply in the locker of the reagents that are needed for the various experiments. Master bottles of each required reagent can be found in the lab on the side shelf or in the hoods. When a particular reagent is called for, thoroughly rinse a dropper bottle, then fill that bottle with the reagent and store it in the locker for the next time it is needed. Label the bottle with name, formula, concentration and date. A lot of lab miles are saved this way. Occasionally a reagent is called for at a concentration that is not available in the lab. That reagent must be prepared by diluting a sample of higher concentration. Recall that as water is added to a solution it becomes less concentrated. The relationship is inverse and is described algebraically as

$$V_cC_c = V_dC_d$$ **Equation 1**

where the c subscripts are for original undiluted values and the d subscripts for final diluted values. Always prepare enough solution to at least fill a dropper bottle.

3. **Weights and Volumes:** Directions for the experiments often call for amounts of materials on the order of ½ gram, ¼ gram, etc. **For the experiments in this section these weights need not be measured on a balance, but can be approximated**. A small reagent spoon gives about one gram of reagent. Volumes may also be approximated **in qualitative experiments** by counting drops. A normal dropper will deliver about 15 drops/mL. Calibrate a dropper if in doubt.

4. **pH Measurement and Adjustment:** pH is a method of measuring the acidic or basic character of a solution. The scale ranges from 0 (most acidic) to 7 (neutral) to 14 (most basic). Proper pH is vital to many of the procedures. It is measured using pH paper which will turn a color characteristic of a certain pH when the paper is moistened with a drop of the solution of interest. A color scale is attached to the vial of pH paper for easy comparison. **The paper is moistened by dipping a stirring rod into the solution, then touching the paper with the wet rod. Do not put the paper into the solution**. Read the test immediately because the color fades out with time. If a solution is not at the proper pH, it can be lowered by adding acid, usually HC1, or increased by adding base, usually NH_4OH, sometimes labeled NH_3(aq). Make adjustment with dilute (6.0 M) reagents a drop at a time.

5. **Precipitation and Centrifugation:** One of the most common techniques for separating out and identifying components of a mixture or solution is by precipitation. If two ions in a solution bond to form an insoluble compound, the compound will appear as small particles. These particles commonly have densities greater than the solvent from which they formed and will settle to the bottom of their container like snow from the sky. **The process is called precipitation**. The solid precipitated compound can be separated from the rest of the liquid by carefully and slowly pouring the liquid into another container leaving the solid behind. **This procedure is called decantation**. The process of separation by precipitation and decantation may be slow because the solid particles are slow to settle. This can be speeded up by using a centrifuge. See Figure 1.

   The centrifuge is a machine in which test tubes can be spun at high rates. Any solid particles suspended in a solution will be driven to the bottom of the test tube by centrifugal force in less than a minute when spun in a centrifuge. When using a centrifuge, be certain to balance the rotor holding a test tube with a second test tube of about equal weight on the opposite side. This avoids vibration while spinning. Vibration can break test tubes, ruining an experiment in progress.

   With few exceptions precipitates are washed at least twice after separation. To wash a precipitate, add a small amount of wash liquid, commonly water, stir up the precipitate, centrifuge, then decant. The first wash liquid is usually saved by adding it to the original solution from which the precipitate was taken. Any second wash liquid is discarded as waste. **Failure to wash precipitates can lead to erroneous results**. Follow the directions of each experiment carefully in this regard.

6. **Heating Processes and Evaporation:** Heat is often required to insure that reactions go to completion. Heating test tubes directly is not advised since overheated liquids can shoot out rapidly causing loss and possible injury or damage. Heat test tubes containing liquids in a water bath instead. (Figure 2) Keep the water bath at a temperature just below boiling or at a very slow boil and keep it hot during the entire period to save time with each use.

   One particular reaction where heat is required is the production of H_2S from thioacetamide for the precipitation of Groups II and III cations.

$$\underset{\text{(thioacetamide)}}{CH_3SCNH_2} + 2H_2O \rightarrow \underset{\text{(acetic acid)}}{CH_3COOH} + NH_3 + H_2S \quad \textbf{Equation 2}$$

H_2S is a poisonous gas with an unpleasant rotten-egg odor. To avoid filling the lab with H_2S gas, cover the test tube of thioacetamide solution **before heating** with a small rubber balloon. This will keep the H_2S contained until heating is finished. See Figure 3. When heating is finished the H_2S will have reacted and the balloon can be safely removed. Save the balloons for repeated use.

When it is necessary to evaporate liquids, do so in a casserole. Direct heating is possible here if done cautiously, to avoid spattering. If very slow evaporation is desired, use a watch glass as the solution container on top of a hot water bath. See Figure 4.

7. **Flame Test:** These tests are an effective way of identifying certain ions in solution. Ions will impart color to a flame when heated directly in the flame. To accomplish a flame test, dip a platinum or Ni-chrome wire into a solution suspected of containing an ion. Place the wet wire into a hot burner flame, entering the flame from the side, and slowly moving the wire toward the hottest portion of the flame. Watch for an identifying color. Be certain the wire is clean before beginning. It can be cleaned by dipping it into 6 M $HC1$, then heating it until no color is given off. Repeat if necessary. Flame colors are hard to remember. It helps to test a known solution just before testing an unknown solution.

8. **Record Keeping:** This topic was treated previously. For qualitative experiments records can be kept in table form. Table 2 illustrates how this can be set up using as an example the analysis of Group I ions.

Table 2 – Analysis of Group I Ions

Step	**Substance**	**Reagent**	**Observation**	**Conclusion**	**Precipitate**	**Solution**
1	2 mL Solution Containing Group I ions	10 drops 6M $HC1$	White Precipitate forms	Ag^+, Hg_2^{2+} or Pb^{2+} possible	$AgC1$, Hg_2C1_2 $PbC1_2$ possible	All other ions possible
2	Precipitate from Step 1	1 mL hot H_2O	Some Precipitate Dissolves	All Group ions Possible Pb^{2+} likely	$AgC1$ and/ or Hg_2C1_2	Pb^{2+} possible
3	Solution from Step 2	4 drops1.0 M K_2CrO_4	Yellow Ppt forms	Pb^{2+} present	$PbCrO_4$	Excess reagents
4	Ppt from Step 2	10 drops 4 M NH_3	Black Ppt forms	Hg_2^{2+} present	Hg and $HgNH_2C1$	Ag^+ Possible
5	So1n from Step 4	6 M HNO_3 to make acidic	White cloudy ppt forms	Ag^+ present	$AgC1$	Excess reagents

Table 2 includes enough information that no additional notes are necessary. It gives materials, procedures, observations and conclusions.