Earlier this semester, you received your general unknown. You distilled it to purify it and to determine its boiling point. You may have also determined its refractive index and density. You also took your unknown through a series of solubility tests designed to tell you a little more about your unknown. If your substance was acidic (carboxylic acid or phenol) you probably know this by now because it was soluble in base. Similarly, you probably know that if your unknown dissolved in acid, it is basic, most likely an amine. And you may have found that your unknown is soluble in water, meaning that your unknown is probably a low molar mass, polar compound capable of hydrogen bonding with water molecules.

More likely than not, however, your unknown did not fall into any of these categories, and you took your unknown into the final solubility test. If it was soluble in or reacted with concentrated sulfuric acid, you now know that your compound is a neutral substance that has an oxygen in it somewhere, an alcohol, ester, aldehyde, ketone, or ether. Or, it may be an unsaturated aliphatic hydrocarbon like an alkene or alkyn. If it was insoluble in or unreactive with sulfuric acid, then you can be fairly confident that your unknown is not one of the oxygen-containing compounds just listed or that it does not have carbon-carbon double or triple bonds. Your unknown is most likely to be an alkane, an aromatic hydrocarbon, or a halogen derivative of one of these hydrocarbons.

So what are you supposed to do during this lab period? Basically, your job is to decide what type of data you wish to purchase to give you further evidence of your structure. Remember, chemical tests can give misleading results. It is not a good idea to begin a series of chemical tests without having some definitive evidence about the nature of your functional group. For example, if you think you may have an alcohol, do not run alcohol tests without first running an IR to verify your assumption. Many students draw inaccurate conclusions and waste a lot of time and chemicals by beginning with chemical tests. Chemical tests are useful for educational purposes to study the reactions you have learned in lecture, but in modern labs they have been replaced by spectroscopy. **So you are required to begin by purchasing data to make certain you are on the right track for the rest of this experiment.**

We do not have the necessary equipment to actually run mass spectra, elemental analysis or carbon-13 NMR on your sample. If you would like to purchase these, write your name, unknown number and what you would like to purchase on a piece of paper. Hand this to your instructor and you will be given a photocopy or printout of the data that you request from files of data that we have for each of the unknowns. **Some instructors may suggest that you email these requests (ms, EA or C-13) prior to the lab day to avoid waiting in line for your data at the start of the lab period.**

Use your time in lab wisely. The handbooks of unknowns are available in the lab. Before leaving you should know the functional groups present on your unknown and have a list of possible candidates you can explore further using your chemical and spectral data.
Pre-lab Preparation

Before coming to lab, you must have done all of the following:

1. Review all of the data you have collected about your unknown so far. This includes physical data, the results of your solubility test, results from any chemical tests you have run on your unknown, and any spectral data you have already purchased.

2. List all conclusions you have drawn about your unknown, based on the data you have reviewed above. These conclusions must be well-organized and neat, but they do not have to be lengthy. They should represent your current thinking about your unknown.

3. List the first piece of data that you will purchase at the start of the lab period. Remember, for mass spectra, elemental analysis or carbon-13 NMR, write your name, unknown number and what you would like to purchase on a piece of paper to give to your instructor at the start of the period. (Some instructors may suggest that you email these requests prior to the lab day to avoid waiting in line for your data).

Experimental Procedure

Safety Considerations

- Review the Safety Considerations sections for the alcohol, hydrocarbon, aldehyde/ketone, and General Unknown I experiments.
- If you are carrying out the Hinsberg test for amines, be careful when working with benzenesulfonyl chloride. It is a skin irritant, especially to sensitive skin around the eyes and nose. Wear gloves and try to avoid getting this reagent on your skin. Wash it off with soap and water if you spill any on yourself. Initially, measure out this reagent in the hood.
- While not a safety hazard, silver nitrate solution, used in a test for alkyl halides, will produce a black mark when it comes in contact with the skin. The mark takes several hours to develop and will rub off in a few days. If you are concerned about possibly spilling silver nitrate on your hands, wear gloves.

In determining the identity of your unknown and reporting it at the end of the semester, there are many types of data that you must collect and report.
1. Physical data:

You probably already have determined the boiling point, refractive index, and density of your unknown. If you have not, then measure them during this lab period. If you are measuring the refractive index, remember to record the temperature as well.

2. Spectral data and elemental analysis (percentage composition data):

Remember that you have a limited budget with which to purchase this information. Think carefully about what to buy. NMR and IR spectra are not always the most useful for the identification of some compounds. You know this from previous unknown spectra that you have tried to analyze. You also know that they are both excellent ways to completely identify others. Mass spectra provide excellent information about certain classes of compounds. Check your discussion notes to find out what classes these are. To obtain a mass spectrum or a elemental analysis (percentage composition by mass) of your compound, request one from your instructor (see earlier notes on how to do this).

3. Chemical tests:

a. After purchasing and analyzing data, you may feel it is necessary to run tests for alcohol, hydrocarbon, or aldehyde/ketones on your unknown. If so, consult with your instructor, explaining why you believe the chemical tests are important in assisting you in the identification of your unknown compound. If your instructor agrees, you may proceed with the chemical tests. Those tests will be available for you during this lab. Refer to earlier procedures in the lab manual for these tests.

b. Alkyl halide tests:

If you have an alkyl halide, these tests may help you determine whether it is primary, secondary, or tertiary. A word of caution is necessary here. In the NaI/acetone test, a precipitate of NaBr or NaCl is a positive test. How fast the precipitate forms will tell you the degree of substitution of the alkyl halide. However, sometimes if an alkyl halide or an aryl halide (e.g. bromobenzene) is added to the reaction mixture as the unknown, a precipitate may form. Rather than resulting from a reaction, the precipitate may be unreacted NaI, forced from solution by the added alkyl or aryl halide which is more soluble in the acetone than the NaI.

As a result, these tests may be helpful or they may mislead. If you think you have an alkyl halide, try the tests, but be wary of their interpretation. You will find more detail about these tests in the “Relative Rates of $S_N1$ and $S_N2$ Reactions” experiment in the CH 203 lab manual. If you did not take CH 203 at Germantown or do not have a lab manual from that course, your instructor will be able to give you a copy of that experiment.
Procedure for Test with Aqueous Silver Nitrate

Into each of three small test tubes, add 2 mL of deionized water and two drops of silver nitrate. Add 5 drops of n-butyl chloride to one test tube and 5 drops of t-butyl chloride to a second. These will be the primary and tertiary alkyl halide standards against which you measure your unknown. Add 5 drops of your unknown to the third test tube. Thoroughly mix the contents of each test tube and observe each for signs of a precipitate. Note the time it takes for each precipitate to form. Write it in your notebook. The shorter the time it takes for a precipitate to form, the faster the reaction was that produced it. If, after 15 minutes, no precipitate has formed in a test tube, heat the tube in a 50°C bath. If, after this time, no precipitate has formed, you probably do not have an alkyl halide.

Procedure for Test with Sodium Iodide in Acetone

Into each of three small, dry test tubes, place 1 mL of NaI/acetone solution. To one tube, add 20 drops of ethyl bromide. To the second, add 20 drops of t-butyl chloride. These will be the primary and tertiary alkyl halide standards against which you measure your unknown. To the third test tube, add 20 drops of your unknown. Thoroughly mix the contents of each test tube. Observe each test tube for signs of a precipitate and note the time it takes for each precipitate to form. Write it in your notebook. The shorter the time it takes for a precipitate to form, the faster the reaction was that produced it. If no precipitate forms, you probably do not have an alkyl halide.

c. Hinsberg Test:

If your unknown was completely soluble in aqueous HCl in the solubility test, you have an amine. (Many people misinterpret this solubility test, so you must purchase data and check with your instructor before proceeding with this test.) The Hinsberg test is a classic test for amines which you should use on your unknown.

The Hinsberg test distinguishes between primary, secondary, and tertiary amines. Unlike alcohols or alkyl halides, the terms primary, secondary and tertiary refer not to the carbon to which the OH or X is bonded but to the number of alkyl or aryl groups bonded to the nitrogen atom. A primary amine has one, the secondary has two and the tertiary has three.

\[
\begin{align*}
R & \quad \text{Primary} \\
R \quad \text{NH}_2 & \\
R' & \\
\end{align*}
\]

Primary and secondary amines can react with benzenesulfonyl chloride to form benzenesulfonamide derivatives which are solid.
RNH₂ + C₆H₅SO₂Cl → C₆H₅SO₂NHR + HCl
R₂NH + C₆H₅SO₂Cl → C₆H₅SO₂NR₂ + HCl

Tertiary amines do not react with benzenesulfonyl chloride because they do not have any hydrogen atoms bonded to their nitrogen atoms. The benzenesulfonamides formed from primary amines have an acidic hydrogen bonded to the nitrogen. They will react with aqueous NaOH to form a water soluble salt which can be regenerated by the addition of aqueous HCl. The benzenesulfonamides formed from secondary amines do not have this acidic hydrogen and will not react with NaOH.

C₆H₅SO₂NHR + NaOH → C₆H₅SO₂NR⁻Na⁺ + H₂O
↓ HCl
C₆H₅SO₂NHR

C₆H₅SO₂NR₂ + NaOH → N.R.

Thus, when an amine is mixed with benzenesulfonyl chloride and aqueous NaOH, several scenarios are possible depending on the type of amine involved.

1º They react to form a benzenesulfonamide which in turn reacts with the base to form a water soluble sulfonamide salt. Acidification of this solution gives a precipitate, the benzenesulfonamide.

2º They react to form a benzenesulfonamide which, because it does not react with NaOH, gives a precipitate of the benzenesulfonamide.

3º They do not react with benzenesulfonyl chloride. Acidification of this reaction mixture dissolves the liquid amine layer. No precipitate is observed at any point.

**Procedure for the Hinsberg Test**

Into a test tube, place 0.3 mL of your amine, 0.4 mL of benzenesulfonyl chloride, and 5 mL of 10% NaOH solution. Stopper the test tube tightly and shake it vigorously for 5 minutes. After 5 minutes of shaking, test the solution with litmus paper to make sure that it is basic. If it is not, add 1 more mL of base and shake for 2 additional minutes. Cool the reaction mixture.

1. If two layers form, separate them and keep the organic layer. Test the solubility of the organic layer in 3M HCl. If the organic layer dissolves, the amine is tertiary.
2. If a solid forms, filter it and put it into a test tube. Add 5 mL of 10% NaOH and shake it vigorously. If it doesn’t dissolve, the amine is secondary. Filter the solid, wash it well with water, and allow it to dry. The product benzenesulfonamide will be a derivative whose melting point will help you to identify your unknown amine.

3. If no solid is formed, and the reaction mixture is essentially one phase, add 3M HCl to the mixture. If a solid forms, the amine is primary. Filter and wash the benzenesulfonamide derivative and characterize the solid by measuring its melting point and comparing this value to literature values.

Post-Lab and Report Requirements

You will submit a general unknown report for this unknown near the end of the semester. Your instructor will give you the date that it is due. It will contain the following information in the same format that you reported other results from previous unknowns: (See Appendix 5.)

1. The number of your unknown.

2. Physical data collected for your unknown and for any proposed structure(s).

3. The results of your solubility test and the conclusions you drew about the classification of your unknown.

4. The results of all chemical tests that you ran on your unknown and the conclusions you drew from each. If you were able to make a derivative, give its melting point.

5. Analysis of all purchased spectra and data.

6. Identification of your unknown, complete with a detailed description of how you identified it from the data you collected.