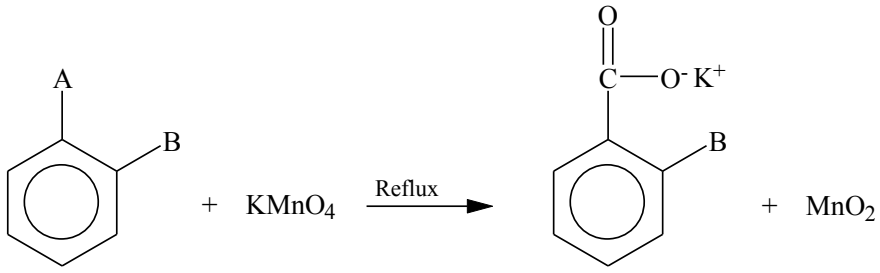
Synthesis and Characterization of an Organic Acid

A Chemistry 121 Laboratory Project

The object of the laboratory exercises in the following weeks will be to synthesize and purify an organic acid, to determine the percent yield of the reaction, and to determine the identity of the acid and starting material. The identity of the acid, and its starting material, will be determined using various physical and chemical determinations. These determinations include: molecular weight of the acid from freezing point measurements, using the solubility and pH of a saturated solution to determine the dissociation constant of the acid, doing a potentiometric titration to determine the equivalent weight and K_a of the acid, determining the melting point of the acid, and using the infrared spectrum of the acid and starting material to help in their identification.

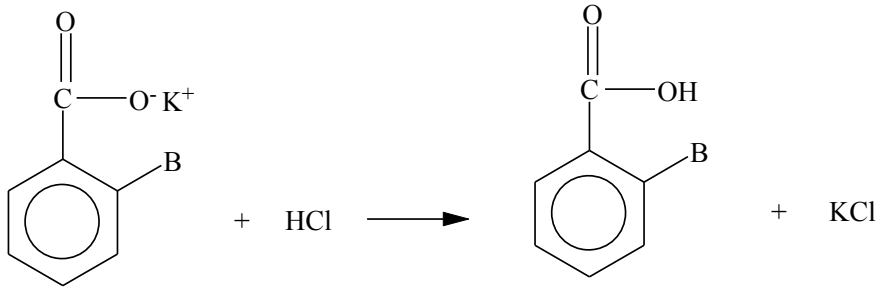
I. Organic Acid Synthesis—CAUTION!!! GOGGLES MUST BE WORN AT ALL TIMES!!!

You will be given one of the following unknown starting materials: benzaldehyde, benzyl alcohol, 2-methoxybenzaldehyde, 4-methoxybenzaldehyde, 2-nitrobenzaldehyde, 2-nitrotoluene, 4-nitrotoluene, 2-chlorobenzaldehyde, 4-chlorobenzaldehyde, 2-chlorotoluene, or 4-chlorotoluene. The structures of these starting materials and their predicted oxidation product are given at the end of this laboratory handout. You will synthesize your organic acid by oxidation of your unknown with potassium



permanganate, $KMnO_4$, according to the following generalized reaction:

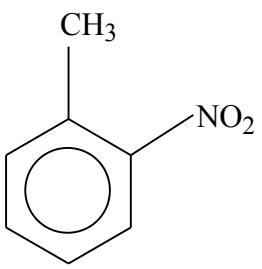
which, after acidification with HCl gives:



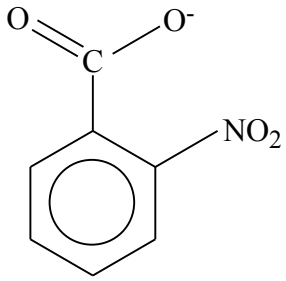
The substituent A may refer to the methyl group, $-CH_3$, the aldehyde group, -CH, or the alcohol group, $-CH_2OH$. The substituent B may refer to hydrogen, H, to the methoxy group, $-OCH_3$, to the nitro

group, -NO_2, or to the chloro group, -Cl.

Prelab Question: Write the complete balanced net ionic equation for the conversion of:



into



with MnO_4^- in alkaline solution

(MnO_2 is the manganese product.)

Procedure:

Set up a reflux apparatus as shown in the model set-up in the laboratory. Place about 4.00 g of the unknown starting material in a 500 ml round bottom flask. Mix about 11.0 g of $KMnO_4$ with 250 ml of water, and, after all of the $KMnO_4$ has dissolved, add this solution to the contents of the 500 ml round bottom flask. Add several boiling chips. Shake well to emulsify the starting material and reflux (boil) gently for up to 1 ½ hours, or until the purple permanganate color is gone. Do not allow the boiling action to become violent enough to eject material from the condenser. The line of condensation may be observed in the condenser and should be in the lower half.

When refluxing is completed, remove any residual $KMnO_4$ (purple color) by adding a few ml of ethanol through the condenser and continuing the reflux for a few minutes. CAUTION: Allow the mixture to cool before adding the ethanol or the system will flash boil. After the $KMnO_4$ has been completely reacted, allow the mixture to cool, and remove the MnO_2 (brown precipitate) by filtering through a Buchner funnel and filter flask. This might have to be done several times in order to remove all of the MnO_2 waste. Place the brown $MnO_2(s)$ in the waste container in the hood labeled "MnO_2 Waste".

Pour the filtrate into a large (>500 ml) beaker and acidify the solution with 6 M HCl until no further white precipitate forms. Filter the crude material with a Buchner funnel apparatus. If acidification does not produce a precipitate, cool the solution on ice to force precipitation. If you still do not have a precipitate, boil down the acidified filtrate until about 50 ml of liquid remains. The bulk of the material should be precipitated at this point. Now you can filter as described above. Carefully collect as much of the product as possible on the filter paper. Place the filter paper and product on a watch glass and place in your drawer until next week. Mass the dry, crude product, to the nearest mg, at the beginning of next week's lab. Record this mass in your laboratory notebook. Use this mass in your percent yield calculation.

Note: Fieser and Fieser's "Techniques of Organic Chemistry", and other sources suggest a way to simplify cleanup by converting the MnO_2 into a soluble Mn species. You should investigate this procedure and report on it as a possibility in your lab report. Make a molecular model or a sketch of your unknown, assuming -B is -OCH_3. How many possible isomers exist?

II. Purification of Your synthesized Acid

The objective of this part of the lab is to purify your acid by a recrystallization technique.

Procedure:

Weigh the crude crystals you synthesized last week. Put them in a 250 ml beaker, add about 10 ml of ethanol, and then bring the mixture to a boil on a hot plate. Once the mixture boils, add a bit more ethanol, if necessary, to dissolve all of the crystals. Now add about 25 ml of deionized water and boil until the volume is back down to about 40 ml, or until a few crystals start to appear on the surface (you want to be sure that all of the ethanol is boiled away). Remove from the heat and filter the hot solution through your stemless funnel using flutted filter paper. Cool the solution on ice and suction filter. Rinse the product with three 5 ml portions of **ice cold** deionized water. Air dry the crystals before setting them in your drawer for next week's lab.

III. Determination of the Molar Mass of Your Synthesized Acid by Freezing Point Lowering.

Prelab Question: What would be the value of K_f for a solvent if 0.800g of salicylic acid, MW = 138.12, dissolved in 10.00g of the solvent caused its f.p. to be lowered by 4.00 ºC?

The object of this part of the synthesis lab project is to determine the molar mass of the organic acid that you synthesized and purified the last two weeks. To do this you will need approximately 20 g of glacial acetic acid, 5 g of salicylic acid, 0.8 g of your synthesized acid, the MicroLAB Interface with temperature probe, and a laptop PC.

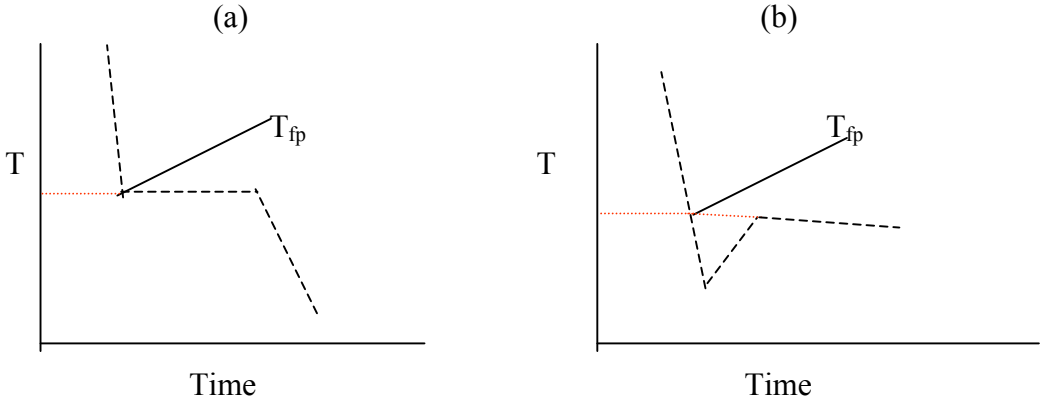
This part of the lab is based on the properties of solutions known as the Colligative Properties. As you remember from lecture, one of the colligative properties is the freezing point lowering of the solvent in a solution relative to that of the pure solvent. The freezing point lowering, ΔT_{fp}, is the difference between the freezing point of the solution T and the freezing point of the pure solvent T_o. The freezing point lowering depends on which solvent is used and on the molality of the solution:

$$\Delta T_{fp} = T - T_o = -K_{fp} \cdot m$$

where K_{fp} is the freezing point constant of the solvent and m is the molality of the solution. This part of the lab consists of three parts: (1) to measure the freezing point of glacial acetic acid, T_o, (2) To measure the freezing point of a solution of salicylic acid in glacial acetic acid of known molality, m. This will allow the determination of the freezing point constant of glacial acetic acid, K_{fp}, through $K_{fp} = \Delta T_{fp}/m$, and (3) The freezing point of a solution made by dissolving a small amount of your acid in glacial acetic acid will be measured, and from this measurement, the molality of the solution can be determined from, $m = \Delta T_{fp}/K_{fp}$. From this molality and the masses of acid and solvent used, you can determine the molecular weight of your acid. This is done using the definition of molality:

$$m = \frac{\text{mol acid}}{\text{kg solvent}} = \frac{\text{mass acid} / \text{MW}}{\text{kg solvent}}.$$

The freezing points of all solutions will be determined by obtaining cooling curves for each solution. Recall that cooling curves can have two basic appearances:



Where curve (a) represents an idealized cooling curve and curve (b) represents a cooling curve with substantial supercooling of the system. In today's lab, expect your cooling curves to look like curve (b) with substantial supercooling.

Procedure:

I. Set up the experiment and read the thermistor calibration file from the calibration folder. In this part you will setup the MicroLAB Interface to take temperature time data and place it in the MicroLAB spreadsheet and on the graph. You may also wish to add the temperature to the digital display. Add the sensors, using the thermistor temperature probe and timer 1.

When you are all set, do a quick practice run: place the thermistor in a small test tube to keep it dry and switching the test tube with the temperature probe between ice and room temperature water to make sure you are getting the correct temperature readings.

II. In this part of the experiment you will determine the freezing point of the solvent glacial acetic acid. Do this by placing ~5 g of glacial acetic acid, massed to the nearest mg, in your 6 inch test tube. Place the temperature probe in the center of the test tube. Now place the test tube containing the glacial acetic acid and temperature probe in the 0^0C water bath and **Start** the experiment. Record the temperature for about 10 minutes while stirring then **Stop**. **Save the data to the hard drive and to your jump drive. You should also export it as a CSV file to your drive**. Now without removing the temperature probe and stirrer from the test tube, heat the solvent above its melting point. Do this by placing your hand around the test tube until the glacial acetic acid melts.

Now repeat the freezing point measurement by Left-Clicking on **Start**. Do a third freezing point measurement if necessary. Save each run on your disk. **Compare your fp (mp) with the literature.**

III. [OPTIONAL: see instructor]
In this part of the experiment you will determine the freezing point constant of glacial acetic acid. To the 5 g of glacial acetic acid contained in your 6 inch test tube add 0.400 g of salicylic acid (MW = 138.12). Obtain the cooling curve as in part II above. Warm the solution as above and obtain a second cooling curve. Do a third run if necessary. Save each run on your disk. When you are convinced that you are through with parts II and III, pour the contents of the test tube into the waste beaker in the hood labeled acetic acid/salicylic acid waste. Note: the fp of this solution should be less than that of the pure solvent. **Compare your K_{fp} constant to the literature. (**See your text book.)

IV. In this part of the experiment you will determine the freezing point of a solution containing the acid that you synthesized. This will enable you to determine its molecular weight. To a clean dry 6 inch test tube add ~5 g of glacial acetic acid, massed to the nearest mg, and then add 0.3-0.4 g, massed to the nearest mg, of small crystals of your acid (you may need to grind the crystals with a mortar and pestle). Place the test tube containing the mixture in a room temperature water bath until it is totally dissolved. Now place the temperature probe and stirrer into the solution and obtain the cooling curve as in part II above. Save your data to your disk. Warm the solution to melt and obtain a second cooling curve. Repeat, if necessary. Save all cooling curves to your disk. After you have thoroughly convinced yourself that you are through with this part of the experiment, pour the contents of the test tube into the waste beaker in the hood labeled organic acid/acetic acid waste.

V. Use the MicroLAB Spreadsheet or Excel to analyze your cooling curves to obtain the freezing point from each run.

1. [From the runs in part III, determine the freezing point constant K_{fp} for glacial acetic acid.]
2. From the runs in part IV, determine the molecular weight of your acid.

IV. Determination of the Equivalent Weight and K_a of Your Synthesized Acid

Prelab Questions: (1) How many grams of KHP are needed to neutralize 40.0 mL of a 0.0900M NaOH solution?

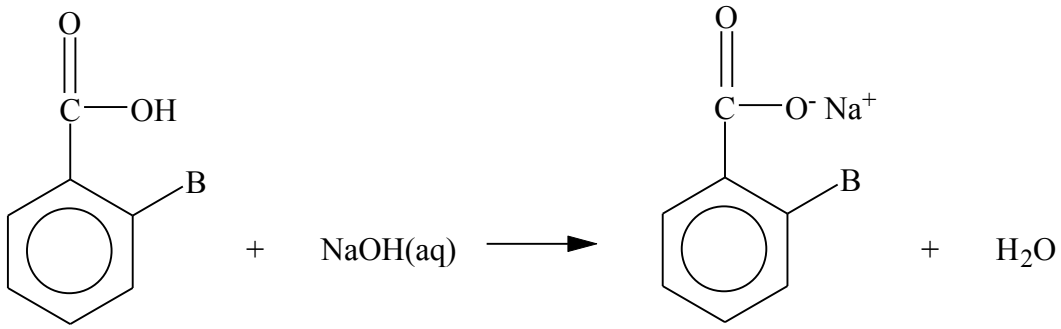
(2) How many mL of 0.0900M NaOH would be needed to neutralize 0.200 gm of an unknown acid whose MW is 135 gm/mole?

(3) Write the structure of the hydrogen phthalate ion.

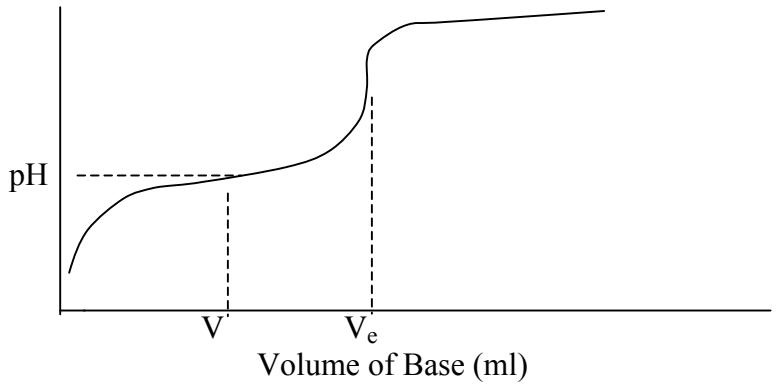
(4) Phenolphthalein is used in titrating KHP with NaOH. Why?

(5) Is phenolphthalein required for a potentiometric titration of a weak acid with NaOH? Why or why not?

The object of this part of the synthesis project is to determine the equivalent weight, or since all the acids produced in this lab are monoprotic, the molecular mass of your acid. You will also determine the value of the acid dissociation constant K_a of your acid. This will be accomplished by performing a potentiometric titration on your unknown acid. The acid-base reaction involved is



From the titration curve generated you will be able to find the molecular mass and the value of K_a. Your titration curve should look like



As you remember from lecture, at the equivalence point of the titration, the moles of acid dissolved equal the moles of base added from the buret, thus the moles of acid added is obtained from

$$\text{moles of Acid} = M_b V_b$$

where M_b is the molarity of the base and V_b is the volume titrated in liters. Thus, from the mass of acid dissolved the molecular weight can be obtained from

$$MW = \frac{\text{mass of acid dissolved}}{\text{moles of acid at equivalence point}}.$$

Now, as demonstrated in class, the pH at any point in the titration is related to the K_a of the acid and to the ratio of the molar concentration of anion to the molar concentration of undissociated acid, through

the Henderson-Hasselbach equation

$$pH = pK_a + \log\frac{[\text{anion}]}{[\text{acid}]}$$

thus, if the molar concentrations of acid and anion are known at a measured pH, the pK_a of the acid can be determined. As can be seen, at a volume of $V = 1/2\ V_e$, the $pH = pK_a$ since [anion] = [acid] at the half way point in the titration. Thus from one titration curve both the K_a and the molar mass can be determined.

In order to find the molecular mass from the equivalence point in the titration you will need base of known concentration, thus this lab will consist of two parts: (1) the preparation and standardization of a 0.100 M NaOH solution, and (2) the potentiometric titration of your synthesized unknown acid.

Procedure:

Part 1. Preparation and Standardization of 0.1xx M NaOH

Prepare 500 ml of approximately 0.100 M NaOH by diluting the appropriate volume of 6 M NaOH located on your laboratory bench. The NaOH can be measured with a 10 ml graduated cylinder and you can dilute the solution in a 600 ml beaker. Check with your instructor to make sure your calculations are correct and you are diluting the proper amount of 6 M NaOH. Transfer this solution to a 500 ml plastic screw top bottle. This NaOH is yours. Do not run out or you will have to start over! Rinse a buret with water, then with 2 ml aliquots of your base, and then fill the buret with your base. Be sure to run some base through the tip so that it is full and then bring the volume of base to the zero mark on the buret. The instructor will demonstrate this for you. Since, in this part, all we are interested in is the precise concentration of the NaOH solution, this is not a potentiometric titration.

Obtain a 125 ml Erlenmeyer flask and weigh it empty to the nearest mg on the top loading balance. Now add 0.4xx g of potassium hydrogen phthalate (KHP, MW = 204.2) to the flask. At your bench add 25 ml of deionized water, 2 drops of phenolphthalein indicator and swirl to dissolve the KHP. Titrate with the 0.100 M NaOH until a pink color persists for at least 30 seconds. Discard the titrated solution in the proper waste container.

Repeat the titration 2 more times with fresh samples of KHP. Compute the molarity of the base from each run and obtain the average. The runs should be reproducible to within 2 %. Do a 4th titration if necessary.

Setting Up the MicroLAB Interface to Measure pH.

In this part you will setup the MicroLAB Interface to take pH and keyboard volume data and place it in the MicroLAB spreadsheet and on the graph. You may also wish to add the pH to the digital display.

You will need to calibrate the pH probe:

Connect the pH electrode to the pH/mV connection on the front panel of the interface. You will need two 50 ml beakers, one containing commercial pH 4.00 buffer and the other containing commercial pH 7.00 buffer. Calibrate the electrode: be sure to keep the solution stirring while you measure pH. Start with pH 4 and finish with pH 7. Rinse (DI water) and dry (KimWipe) the electrode between measurements. Ideally, there should be about a 180 mV difference between the pH 4 and pH 7 buffer, and the slope of the calibration line should be about 60 mV/pH or 0.017 pH/mV. Be sure to save the results to the correct file.

Place the pH electrode in pH = 4 buffer between runs. Do not let the electrode dry out.

Part 2. Potentiometric Titration of your unknown acid using the MicroLAB Interface.

Dissolve 0.200 g of your unknown acid in 50 ml of warm DI water. Place the stirring bar and pH electrode in the solution. Turn on the stirrer to a slow speed and make sure it does not bang against the pH electrode. Now position the buret containing your standardized NaOH solution into the beaker so that the tip is just above the solution and oriented such that you can turn the stopcock on the buret.

L-Click on **Start** and enter 0 mL to measure the initial pH. Now add 0.2 ml of base, wait a few seconds for the pH to stabilize, and enter 0.2 from the keyboard and press **Enter**. Continue adding NaOH in 0.2 ml increments until you have passed the endpoint of the titration. Be sure to enter the Total Volume Added with the keyboard after each addition of base. Once past the endpoint you can add base in 0.5 ml increments then in 1.0 ml increments until the pH = 12 or you have added 30 - 35 ml of base. The important parts of the titration curve are the plateau as well as the end point. Stop the experiment and **save the data to the hard drive and to your own jump drive**. Discard the titrated solution in the proper waste container labeled organic acid titration waste, located on the side table.

Repeat with a new sample of your unknown acid. It is a good idea to recalibrate the interface in the pH 4.00 and 7.00 buffers before you begin. Make a third run if necessary. Be sure to save the data in each of your runs to your disk under separate names.

If you do not have enough unknown to do two runs, see the instructor for instructions on how to jump out of the window.

Before you leave lab, insert a titration curve into your lab report draft and calculate individual and mean values for the equivalent weight and K_a. You should include a titration curve for your unknown, and sample calculations for the determination of K_a and the equivalent weight in your formal laboratory report.

V. Determination of the Melting Point.

If a material is pure, melting occurs over a very narrow temperature range, and the solid is said to have a "sharp' melting point. This melting point is of considerable importance in identifying your solid acid, because it is unlikely that other compounds will melt over exactly the same temperature range. An impure sample of the same substance melts at a lower temperature and over a wider range in temperature due to the freezing point lowering of the solvent by a solute. In this part of the experiment you will measure the melting point of your solid acid in order to help in its identification.

Procedure:

A Mel-Temp melting point apparatus will be used to determine the melting point of your synthesized acid. The instructor will demonstrate the use of this instrument.

a. In order to use the Mel-Temp apparatus, you must place each sample in a melting point capillary tube. To do this, introduce a small amount of powdered sample into the capillary tube by pressing the open end of the tube vertically into the solid. Then gently tap the tube on a hard surface to bring the solid to the sealed end of the tube. Repeat this process until you have about a 1 cm length of sample in the tube.

b. Do a practice melting point on a sample of benzoic acid, which should melt at 122 ^{o}C. If you are doing it right, you will hit the melting point of the known pretty close and sharp, lending confidence to the unknown results. Keep in mind that the heat capacity of the thermometer probe is much greater than the milligram size sample in the capillary. As a result, the capillary will respond to changes in temperature much more quickly than the thermometer – so go **SLOWLY** as you near the melting point if you hope to get a temperature reading that is anywhere close to that of the sample. About 1 ^{o}C/minute is good near the melting point.

c. Fill a capillary with your unknown acid and determine its melting point as you did in the practice run. Repeat the melting point determination.

Compare the melting point of your acid with those of the possible products. These are given with the product structures at the end of this handout.

VI. Infrared Spectrum of Your Acid and its Starting Material.

Of all the properties that can be used to identify an organic compound, one of the most useful is the infrared spectrum of the compound. An infrared spectrum is a plot that shows how much infrared radiation is absorbed by a material at each wavelength of light that is passed through the sample. The infrared spectrum is due to the vibrational motion of the molecule. The allowed vibrational motions of a molecule are a result of the structure and composition of the molecule. Molecules that have different structures and compositions have different vibrational spectra. Thus, the IR spectrum is like a "fingerprint" of the compound and can give a great deal of information about its structure.

A molecule is constantly vibrating, with its bonds stretching and contracting and bending with respect to each other. Changes in vibrations are caused by the absorption of IR radiation. the energy of this radiation is usually expressed in wavenumbers, cm^{-1}, which is the reciprocal of the wavelength expressed in centimeters. It is a measure of the number of light waves per centimeter. Thus an infrared

spectrum is just a plot of the absorption of radiation as you "scan" through the infrared region of the electromagnetic spectrum.

In this experiment, you will obtain the IR spectrum of your synthesized acid and of your starting material. These spectra will be compared with spectra of known compounds contained in an IR spectrum library. It is assumed that the library spectrum that best fits the spectrum of your compound represents the identity of your unknown. **Beware:** If the IR spectrum of your compound is not in the IR library, the spectral search will still give the best fit spectrum that is contained in the library. Also, if your compound is not pure, i.e., a mixture, the spectral search will assume a pure compound and still give you a best fit of your spectrum to those in the library. Thus you must use caution when using spectral searches to identify a substance.

Procedure:

The technique of obtaining an IR spectrum of a compound depends on the physical state that the substance exists in at the temperature the spectrum is being obtained. In this experiment we will be dealing with liquids and solids. The sampling methods that will be used for these states are:

a. Liquids will be analyzed by placing a small drop of sample on a AgCl disc, and then placing a second AgCl disc over it, forming a thin layer of liquid between the plates. This system will then be placed in the Nicolet FTIR Spectrometer, and the IR spectrum will be obtained. AgCl is completely transparent in the IR region, even though it appears colored in the visible.

b. Solids will be analyzed using the diffuse reflectance technique. This method involves mixing your sample with KBr, placing it in the diffuse reflectance apparatus, and then obtaining the IR spectrum. For our system you are to mix 5 mg of your acid, or starting material, with 500 mg of KBr. This mixture is then placed in the "Wiggle Bug" to mix, and then placed in the sample cup in the diffuse reflectance apparatus. The IR spectrum will then be obtained.

Since there are several compounds that absorb IR radiation in the sample path, i.e., water, CO_2, and impurities in the AgCl and KBr, their spectra must be subtracted out. This is done by obtaining a background spectrum of the system without the sample and then subtracting this absorbance spectrum from the sample spectrum. This subtraction is done automatically by the software when the sample spectrum is taken.

The instructor will show you how to use the IR Spectrometer and how to search the spectral libraries. All spectra are to be saved on your flash drive. Spectra will either be plotted when your spectra are obtained, or you can plot them out later using the WinFirst software in the Computational Chemistry Laboratory. Both sample and best-fit spectra should be plotted so you can display and talk about them in your lab presentations.

A good idea would be to copy the FTIR spectrum and paste it into a word document (as a bitmap?) so that it can be incorporated easily into your lab report. The same is true of the library search results.