Title: **Determination of the Identity of an Unknown Compound**

New tricks: A1 through A5, B1, C2, D3, E1, F1, F3, and F8

New Principles: Recrystallization, determining melting points, IR and NMR spectrometers

Instrument Operation: Fisher-Johns and MeltTemp melting point apparatuses

Introduction:

Time for a puzzle! In this experiment you will learn how to purify a compound, measure its melting point, and record data in the form of "spectra" that can be used to identify it. The experiment is in three parts. In Part I you practice with a known compound, benzoic acid. In Part IIa you purify a compound you don't know the identity of (an "unkown"), record its melting point and spectra, and use that information to figure out what it is. In Part IIb you analyze by NMR spectroscopy a commercial product of your choosing. *You will not finish this experiment this week*. In fact, you should not expect to finish this experiment much before the end of the semester.

Part I: Recrystallization

Throughout your work in Chemistry 253 and 254 you will synthesize products that are solids at room temperature. Such products often are contaminated with impurities, which could be unreacted starting materials, by-products, or the solvent used to run the reaction. One technique that chemists use to accomplish the separation of desired crystalline product from various impurities is recrystallization. Your success in organic laboratory will depend in large measure on your ability to perform recrystallizations to yield highly purified products. Acquisition of good recrystallization skills at the very earliest stage of this laboratory course will ensure good results later on.

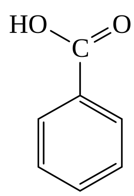
Recrystallization involves dissolving a "crude" solid in a **<u>minimum</u>** amount of hot solvent in order to produce a saturated solution. Upon cooling, the solution becomes supersaturated, and crystalline material usually precipitates out of the solution. Suction filtration is used to collect the precipitated crystals.

The technique of recrystallization draws from what you learned in first-year chemistry about enthalpy and entropy. As a supersaturated solution of a compound cools, a crystal lattice forms, excluding impurities that may exist along with the original "crude" material. Ideally, all the impurities remain in solution and the resulting crystals contain only the desired product. **Crystals form best when they form slowly!** If cooling is rapid (i.e., if you plunge a warm saturated solution into an ice-bath), the crystal-forming process becomes so rapid that it may cause impurities to be trapped into the crystal matrix; such impurities would not be present if slow cooling were allowed to occur.

One way to assess the purity of a solid material is to determine its melting point. If the melting point of a compound is already known after searching the chemical literature, then the chemist can compare the melting point he or she obtained with that already observed. Clearly, if the observed melting point and the "literature" melting point agree, then one has a good indication that the identity of the compound obtained from experiment matches that already known from the literature.

Melting Points Are Ranges It is essential to report the melting point range when reporting a melting point value. Materials typically do not melt at a single temperature; they melt over a range of temperatures (See **Principles: Melting**, page P-3, for a discussion of melting point ranges and purity). Generally, the smaller the melting point temperature range, the purer the crystals. A melting point range of less than 1^{o} C is usually a good indication that the material being tested is highly pure.

Recrystallization is an Art In this experiment you will practice the art of recrystallization by first purifying a sample of benzoic acid, which has a reported melting point of 122.0-122.4^{o} C.



Benzoic Acid

Solvents Make a Difference You should use at least two different solvent systems in your recrystallization attempts, striving to produce the maximum yield (as determined by the amount you obtain compared to the amount you recrystallized) and maximum purity (as demonstrated by the narrowness of melting point range, also termed the sharpness of the melting point). Realize that the best solvents for recrystallization are only moderately polar. If the solvent is too polar, the compound may be too soluble when cooled, so although it will go into solution, it will never come out. Water and ethanol are very polar solvents. Solvents that are too nonpolar may not allow the compound to dissolve at either temperature. Hexane and ethyl ether are relatively nonpolar solvents. Sometimes a mixture of polar and nonpolar solvents works best.

Part IIa – A Sample of Our Choice

In this part of the experiment you will receive an unknown compound and try to identify it on the basis of its melting point, solubility, and spectral properties. One of your goals will also be to **recrystallize** the unknown to provide the maximum amount of material with the sharpest possible melting point.

Mixed Melting Points Generally when two different compounds are mixed, their melting point is lower than either individually. A very good test of purity, then, is to mix the compound you have with an equal amount of the compound you *think* you have. If the "mixed" melting point is the same for either alone, that is an excellent. You might want to consider doing this at some point with your unknown.

Part IIb – A Sample of Your Choice

In this part of the experiment you will take any sample you want – provided it can dissolve in water or chloroform – and analyze it by NMR spectroscopy.

Green aspects:

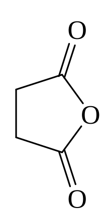
Benzoic acid and the unknown compounds used in this experiment are generally considered to be relatively non-toxic. Some of the unknowns are listed as "irritants," and thus you should handle all compounds carefully. The solvent systems (often water-based) that you may use in this experiment are relatively environmentally-friendly and are typical of solvents used in green chemistry.

Pre-Lab Questions:

1. Compare the shape of an Erlenmeyer flask to the shape of a beaker. Instead of using an Erlenmeyer flask for recrystallization, a student tried to recrystallize a solid by heating both solid and solvent in a beaker. Soon the student discovered a layer of solid covering the bottom of the beaker, and the solvent was all gone. What happened here? Was the solid on the bottom of the beaker recrystallized? Why would using an Erlenmeyer be a better idea?

2. Why is it important to allow crystals to sit out open to the air for some time to"dry" before taking their melting point?

3. Benzoic acid and succinic anhydride have almost identical melting points, even upon recrystallization. Propose a method you could use involving solubility and chemical properties that would clearly distinguish the two compounds. [Hint: Look at sections **1.16** and **1.17** in Bruice's *Organic Chemistry*.]



Succinic Anhydride

In Your Laboratory Notebook:

Observations In this and all future experiments, be sure to take good notes while you work. It must be clear to the reader what you did WITHOUT REFERENCE to the laboratory manual. Read carefully all of the material in **Tricks of the Trade: A1 through A5.** Imagine that the reader must repeat your work having only your laboratory notebook for reference. Don't worry if you don't catch on immediately. This takes practice!

Analysis Summarize all of your observations relating to solubility, melting points, and spectra. Identify your compound, including full IUPAC name, CAS Registry number, structural drawing, and molar mass. Compare the melting point of your compound with the one you find in the literature. (The Merck Index, Dictionary of Organic Compounds, or Aldrich Catalog are good references for this. It's fine to look this up on the web, but please provide a book reference as well.) If you take a mixed melting point, report those results. Obtain at least two types of C13 NMR spectra, an H1 NMR spectrum, and an IR spectrum. Discuss each spectrum taken, indicating how each agrees with the structure you have proposed. For IIb obtain at least an H1 NMR spectrum and discuss it with your instructor and summarize what the H1 NMR tells you about it.

Discussion and Conclusions. In Part IIa, what is your compound? Using SciFinder Scholar, find references to this compound using its CAS registry number. Discuss at least two references. Is it used medicinally, for example? If so, how? In Part IIb, what does NMR spectroscopy tell you about your sample?

Procedure:

<u>Part I</u> Weigh out about 200 mg (it could be 195 or 205 mg, but you do need to know the exact mass) of benzoic acid, and add this material to a 50 mL Erlenmeyer flask. Add 5 mL of deionized H_2O to the flask and heat the mixture carefully on a **hot plate**. Continue adding water (see **Trick of the Trade E1**) until the benzoic acid just barely dissolves in the hot H_2O (add water in 1 mL increments). Carefully remove the flask from the hot plate and set aside for cooling.

Allow the flask to cool to room temperature and observe if crystals form. If so, place the flask in an ice bath and allow the contents to cool to 0 ^{o}C. Collect the crystals that form by **suction filtration**, using a Buchner funnel and washing the crystals with ice-cold H_2O. Place the crystals on a pad of three or four pieces of filter paper (11 cm) and use a spatula to move the crystals around on the paper. This action will speed the drying process. When the crystals seem dry and fluffy (this could take up to a week of drying in the air), determine their mass and **melting point**. Determine the **percent yield**. Report these data in your notebook.

<u>Part IIa</u> Recrystallize about 200 mg of an unknown compound twice, using two different solvents or solvent combinations. Please note that you may have to try more than twice in order to get good results (nice crystals with a sharp melting point). Given below is a list of possible compounds that your unknown might be.

Note: The 5 mL you used for benzoic acid was an appropriate amount for that solvent and that compound only; for your unknown, start with 1 mL of any solvent you try and add more only if necessary.

In your notebook describe all your observations, including details (amount of compound, amount of solvent, amount of product collected, percent yield, mp range, etc.) for all attempts at recrystallization, even if the solvent you chose did not give you good results.

<u>Part IIb</u> Bring to lab some commercial product – a beverage, a nonprescription drug – anything that will dissolve in water or chloroform (a fairly polar organic solvent). After confirming with your instructor that it is appropriate, obtain at least an H1 NMR spectrum (perhaps more, if you want) and discuss them with your instructor.

<u>NOTE:</u> *Treat the process of identifying your unknown as an ongoing experiment to be preformed over the course of the semester. As you obtain IR and NMR spectra, discuss them with your lab assistant and instructor. Discussion of IR and NMR spectra need to be part of your analysis.*

LIST OF POSSIBLE UNKNOWN COMPOUNDS USED IN THIS EXPERIMENT

Compound	Melting point / ^oC
p-acetanisidide	128-130
p-acetotoluidide	149-151
benzamide	130-131
benzanilide	164-166
benzoin	135-137
benzilic acid	150-153
p-bromoacetanilide	167-169
p-bromobiphenyl	90-92
caffeine	234-236
N,*N*-dimethyl-*p*-aminobenzaldehyde	70-75
fluorine	114-116
hippuric acid	188-191
2-methoxynaphthalene	73-74
methyl *p*-nitrobenzoate	94-96
trans-stilbene	122-124