

1. Crystallization

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C.N. Hammond, 21-28 (lab notebook and % yield)
and P.F. Schatz: 183-197 (recrystallization)
174-183 (melting points)

Vocabulary: Solute	A compound which is dissolved in another compound and present in a lesser amount.
Solvent	The compound which is present in the excess. It is capable of dissolving a solute but not reacting with it.
Miscible	Two or more compounds, which dissolve in one another to form a homogenous solution are said to be miscible.
Filtration	A process by which one material is separated from another based on differences in particle size.
Trituration	Repeated washing of a solid with a solvent.
Solubility	The degree of which a compound dissolves.
Melting point	The temperature range at which a compound melts from the observation of the initial melting of the first to the last crystal.
Filtrate	The material that passes through the filter and remains in the receiving flask. It is sometimes referred to as the <i>mother liquor</i> .
Aliquot	A small amount of a liquid, which is either added to or taken from a solution.
Reflux	Heating a solvent/compound to its boiling point. It is evident from the condensation of that liquid on the walls of the container.

This procedure and material has been adapted from the microscale procedure described in *Macroscale and Microscale Organic Chemistry Experiments* by Kenneth L. Williamson and *Experiments in Organic Chemistry* by Louis F. Fieser.

In a nutshell:

Recrystallization is a technique used to purify a solid. We use it to purify starting materials as well as the products of a reaction. Once a solid is isolated at the end of a reaction, then we dissolve it with the smallest amount of solvent (liquid) as possible. In theory the impurities will stay in solution (or be filtered), while the “pure” material will slowly crystallize out leaving the impurities behind.

Background

What is crystallization? According to the *American Heritage Dictionary of the English Language* (American Heritage Publishing Co, and Houghton Mifflin Company, Boston, 1973, pg 319), a crystal is "a three-dimensional atomic, ionic, or molecular structure consisting of periodically repeated, identically constituted, congruent unit cells" and crystallize is "to cause to form crystals or assume a crystalline form". There are examples of crystalline solids, which we run across in our everyday lives. Salt (NaCl, ionic solid) and sugar are typical examples of crystalline solids. As organic chemists, we use recrystallization as a technique to purify either a desired product or a starting material. If you start with a compound that is pure, you have a greater chance for your reaction to succeed.

In crystallization, it is necessary to consider the properties of the solvent. The reason why is because organic chemists usually say that *like dissolves like*. Therefore, chemists look to select solvents for recrystallization that have structures similar to the solute. In organic lab, you will be using solvents like water, toluene, and hexanes. Water contains networks of hydrogen bonds. It easily dissolves ionic solids, such as NaCl, and polar compounds, such as alcohols (R-OH). Toluene is an aromatic solvent, which contains a benzene ring, so other aromatic compounds should also be soluble in it. Hexane is an aliphatic hydrocarbon, so it would be expected to dissolve hydrophobic compounds.

In general, there are seven possible steps for the recrystallization of a compound. In some cases you would use them all. They are:

- Choose a solvent.
- Dissolve the solute (your compound).
- Decolorize (to remove any colored impurities).
- Filter (to remove any insoluble impurities).
- Crystallize (usually by cooling the solution).
- Wash the product (rinse the desired crystals).
- Dry (to remove the solvent).

The first step, finding a suitable solvent, is sometimes the most difficult one. Why? Well, you want to choose a solvent that will dissolve the solute at temperatures higher than room temperature. If the material goes into your solvent at room temperature, then you will never be able to recover your compound. That is not a good thing if you are being graded on % recovery or yield. Ideally, the solubility of the solute should be at its maximum in the hot solvent and at its minimum in the cold solvent. A good solvent will have the property will dissolve 18 g/100 mL of solvent at its boiling point but 0.5 g/100 mL at ice water temperature (0 °C). In some cases, you will not be able to find a great solvent for recrystallization so you will have to use a two-solvent or mixed solvent pair. This technique will be discussed in your procedure, but essentially you need to use two solvents that are miscible in one another (i.e., they dissolve in one another). One such mixed solvent system is ethanol (ethyl alcohol) and water. The general rule is *like dissolves like*. Once you have chosen a solvent (or solvent system), then you dissolve your solid in your chosen solvent system. Never add more than 10 mL solvent per gram of solute. Also, whenever you heat a liquid, you must use either a boiling chip or boiling stick. Otherwise, the solution may superheat and “bump” (or boil out all at once).

The third step is important if you know that your compound should be colorless/white but isn't. Unfortunately, most organic compounds are colorless. If necessary, we use a decolorizing agent, which is usually charcoal. Colored compounds/impurities are large, aromatic compounds, which then stick to the charcoal. The fourth step is to filter away the impurities, which may include the charcoal. It is necessary that the solution is hot for this step so that the crystallizing solid does not hinder the filtration.

Then, the solution is cooled to room temperature and sometimes even colder with the aid of an ice-water bath. The best crystals come from letting the solution cool slowly so that the impurities are not trapped again

in the solid. Once the crystallization step is complete (no more crystals are formed), the crystals are filtered and washed with a small amount of the solvent. It is necessary to let the crystals dry so as to get rid of the solvent. This is important in the determination of the melting point and the % recovery of the compound. If you were to have a % recovery or yield of over 100% than you probably have solvent in your crystals. Sometimes, instead of crystals, you may see an oil. This process is called "oiling out". It may be due the compound's insolubility, the melting point is lower than that of the solvent, or that the compound is cooled too quickly.

You will be taking melting points to identify your unknown compound. What is a melting point? Well, it is the range of temperatures over which a compound melts. The range begins with the observation of the melting of the first crystal or first drop and ends at the completion of the melting of the material. That definition seems a little subjective but you will see that it is not. Also, it really is a range rather than a single point because the melting of a solid takes place over some time. According to our technique book, if you see only one point listed, it is probably the high end of the range. Although the procedure for taking a melting point measurement appears simple, samples must be prepared with care. If a compound is not dry (if it contains the solvent of recrystallization), the melting point will be low and/or broad. If the compound is impure and that impurity is soluble in the compound, you will observe the same effect. If you heat the compound too quickly, then there will be an error introduced into the melting point reading.

In this experiment, you will be performing five one-step reactions, isolating the product, and then recrystallizing the solid from either water or an ethanol/water (solvent pair). You will take the melting point of the solid that you are assigned and report all weights.

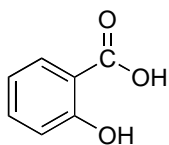
Melting point assignments are as follows according to the first letter of your last name:

<i>Part</i>	<i>First letter of last name</i>	<i>Record melting point of</i>
1	A-H	salicylic acid
1	I-P	benzoic acid
1	Q-Z	phthalic acid
2	A-M	naphthalene
2	N-Z	biphenyl

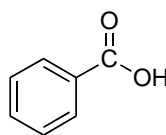
Experimental

There are two different parts to this experiment.

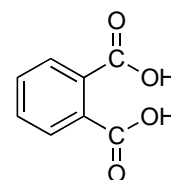
Part A. Recrystallization of Salicylic Acid, Benzoic Acid and Phthalic Acid from Water



Salicylic Acid



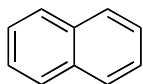
Benzoic Acid



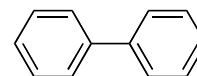
Phthalic Acid

Place approximately 200 mg of salicylic acid into a 50 mL Erlenmeyer flask. Add approximately 2 mL of hot water (dropwise) to your solid and a boiling stick and heat to reflux on a hotplate. Remove the flask from the hotplate to see if the entire solid is dissolved. If not, add more hot water and heat back to reflux, and then remove from the heat. Repeat until the entire solid is dissolved. Mark the solvent line on the flask with a Sharpie. Let cool to room temperature, place in an ice-bath for ten minutes, and vacuum filter. Wash with cold water to remove any solid residue. Determine the volume of water used by filling the flask to the Sharpie line and then transferring the water to a graduated cylinder. Record the volume of water used in your notebook. Weigh the recrystallized solid. Record the melting point of your solid if you were assigned this compound. Repeat this procedure for both benzoic acid and phthalic acid.

Part B. Recrystallization of Naphthalene and Biphenyl from an Ethanol Water Solvent Pair



Naphthalene



Biphenyl

Place approximately 200 mg of naphthalene into a 50 mL Erlenmeyer flask. Dissolve (dropwise) in a slight excess of refluxing ethanol. Remove from the heat and add water dropwise while swirling until the solution remains slightly cloudy. Reheat to reflux. If the solution does not go clear, add ethanol dropwise until clear. Let cool to room temperature, place in an ice-bath for ten minutes, and vacuum filter. Wash with cold ethanol to remove any solid residue. Weigh the recrystallized solid.

Record the melting point of your solid if you were assigned this compound. Repeat this procedure for biphenyl.

For both experiments:

Record the results in your notebook, including amounts of material used, amounts of solid recovered, volume of water used in Part 1 and melting points as assigned.