

“Blessed are the pure in crystal”

Merrit DeBartolo 2002

It is possible to purify compounds by recrystallizing them in a solvent in which they are soluble at a high temperature but insoluble at a low temperature. The target compound dissolves in the solvent at high temperatures allowing the researcher to filter out insoluble impurities. At low temperature the target compound forms crystals and precipitates out of solution while the soluble impurities remain dissolved.

Impure crystalline (solid) substances can be purified by recrystallization from a suitable solvent. This process depends on the observations that:

- 1) most compounds are more soluble in hot solvents than in cold ones and
- 2) impurities (such as sand and dirt) are likely to have solubilities different than the desired compound.

The technique by which a solid compound is purified by its characteristic solubilities is called recrystallization. Recrystallization involves:

- a) dissolving the impure material in a minimum amount of boiling solvent,
- b) filtering the hot solution to remove any insoluble impurities,
- c) allowing the solution to cool and to deposit crystals of the compound,
- d) filtering the crystals from the solution that may contain dissolved impurities and
- e) drying the crystals.

If recrystallization is to be effective, the solvent must be properly selected.

A good recrystallization solvent should:

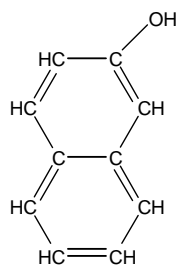
- 1) dissolve a moderate quantity of the target substance near its boiling point but only a small quantity near 0 °C,
- 2) not react with the target substance
- 3) dissolve impurities readily at low temperatures or not dissolve them at any temperature and
- 4) be readily removed from the purified product.

Wynken, Blynken and Nod one night  
Sailed off in a wooden shoe -  
Sailed on a river of crystal light,  
Into a sea of dew.  
**Eugene Field**

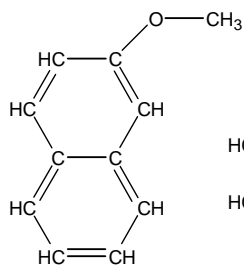
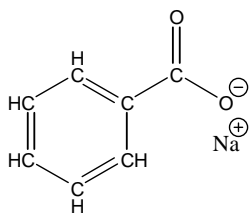
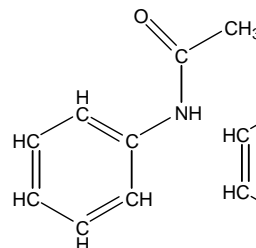
"The Organic Chem Lab Survival Manual" by J.W. Zubrick on reserve in the library has a chapter on recrystallization (Chap 13).

**Part I.**

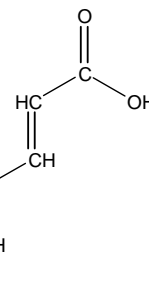
We will explore the solubilities of five standard compounds in three solvents of differing polarity.



2-naphthol

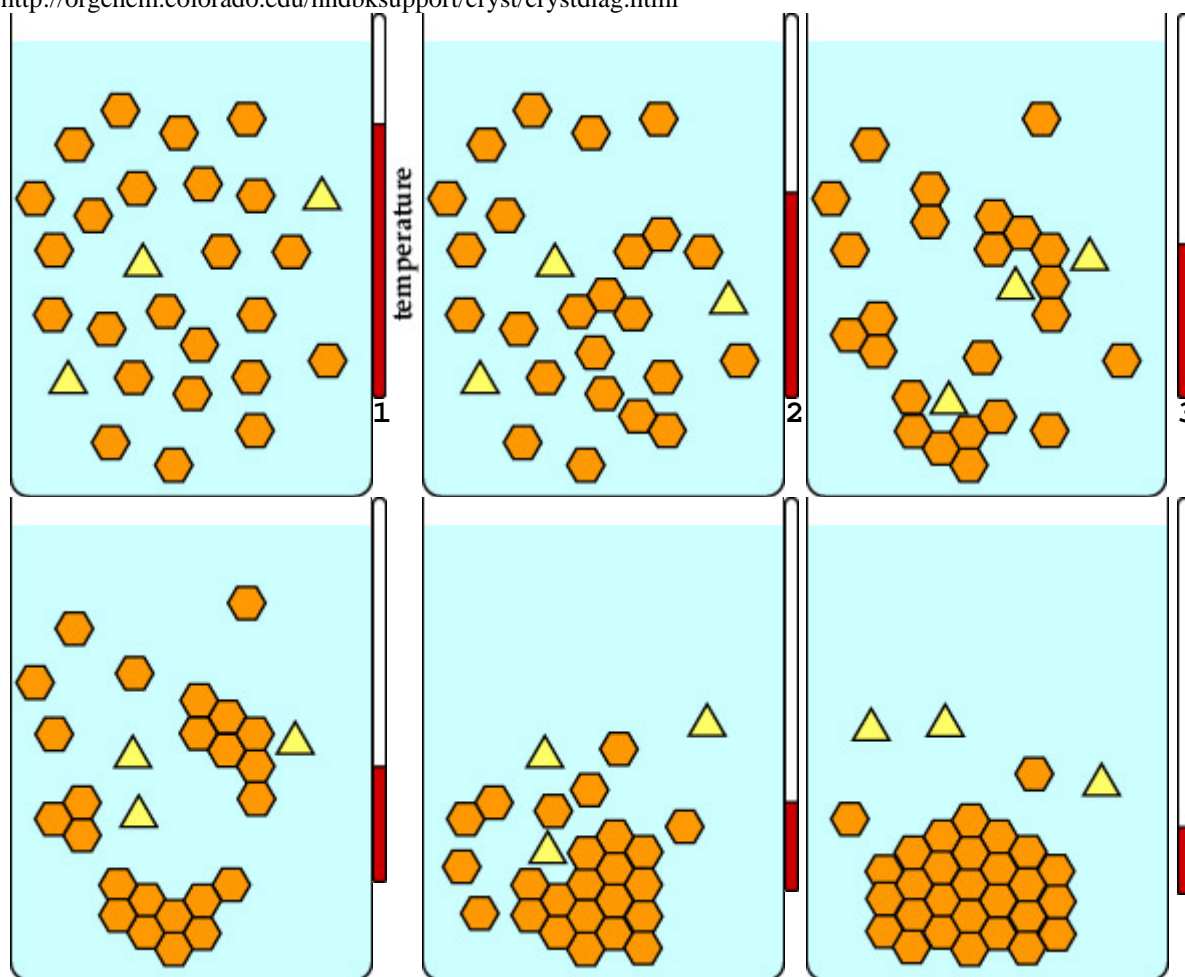
2-methoxy  
naphthalenesodium  
benzoate

acetanilide



cinnamic acid

<http://orgchem.colorado.edu/hndbksupport/cryst/crystdiag.html>



**Part I.**

Obtain mass of dried solid from Experiment #2.

**You may do "part I" in groups of two or three. Each student must perform at least 5 experiments.**

Start some water boiling on a hot plate.

Obtain at least 15 mL of each of the three solvents: water, ethanol and hexane.

For each of the five compounds:

1. Put a small amount (about 0.10 gram) of the compound in a large test tube.
2. Add three mL of solvent to the test tube. Label the test tube. (sticky label or marker)
3. Mix the contents by swinging the bottom back-and-forth while keeping the mouth steady.
4. Record your observations on the solubility of the compound in the solvent at room temperature. Share your results with your partner(s).
5. Heat the tubes in a hot water bath (75-99° C). You may stand up several tubes in a 400mL beaker half-full of water. Record the temperature of the water bath. Record your observations on the solubility of the compound in the solvent. Share your results with your partner(s).
6. Allow the tube to cool to room temperature while you prepare the rest of the experiment. Record the temperature of the room. Record your observations. Do solid crystals form? Share your results with your partner(s).
7. Cool the tube in an ice and water bath – Use a 400 mL beaker so they won't fall over. Record your observations. Record the temperature of the ice bath. Do solid crystals form? Share your results with your partner(s).

Observation key:

vs = very soluble = dissolves completely with little or no mixing

so = soluble = dissolves eventually if you shake it enough.

ss = somewhat soluble = only part of the solid dissolves after shaking.

in = insoluble = none of the solid appears to dissolve.

**Part II. Recrystallization of Unknowns**

Based on your knowledge of physical and chemical properties that you gathered from TLC, extraction experiments, and the solubility tests you will conduct in this experiment, you will have to select a solvent and recrystallize the two components that you isolated from the liquid/liquid extraction of your unknown mixture.

1. Place small, approximately 0.1 gram of one of the solids in 3 large test tubes.
2. Select three solvents that you feel might be suitable solvents for recrystallization, and add about 3 mL of one of the solvents to each of the test tubes.
3. Agitate the solutions for a few minutes and then observe which solvents dissolve the compound at room temperature. (These are obviously not suitable solvents for recrystallization.)
4. Heat test tubes that contain solid in a hot water bath. If, after a few minutes, the solid does not dissolve add more solvent.
5. Allow tubes to cool to room temperature. Continue cooling in an ice bath. Observe which solution gives the best crystals. If a colored impurity is present it should appear to remain in solution.
6. Repeat the solvent selection process for the second solid substance.

An ethanol/water mix might be just the thing you need. Ethanol and water dissolves like an alcohol at high temperatures and like water at low temperatures. Dissolve your unknown in hot ethanol and then add hot water until the solution gets a bit cloudy. Cool it off and voilà, crystals!

**Now you are ready to recrystallize your unknowns!**

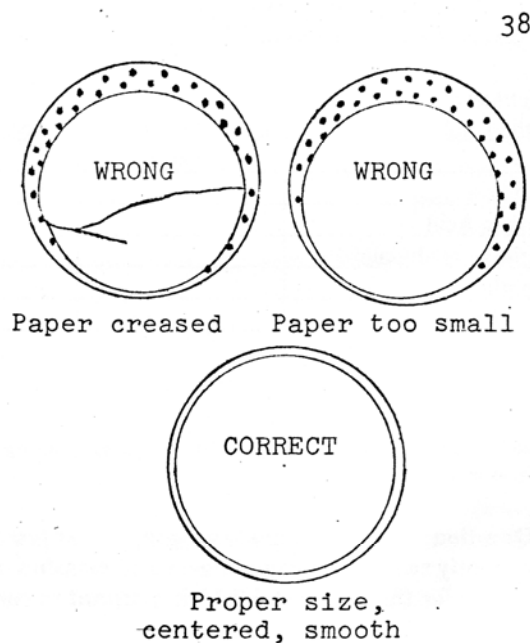
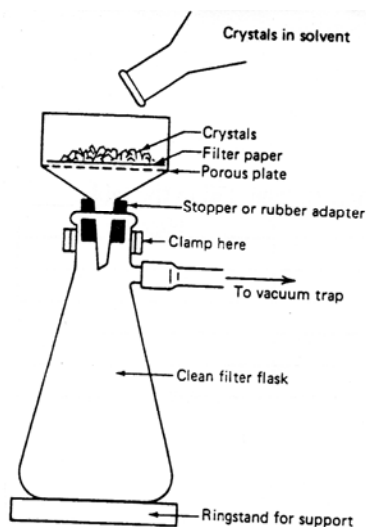
7. Recrystallize your unknown solids from the solvents you selected. Weigh each sample before you start.
8. Dissolve your unknown in a minimum amount of solvent. Add a small amount of solvent and heat. Add solvent until the solid dissolves. Use one of your small beakers.
9. Allow the solution to cool to room temperature. Continue cooling in an ice bath.
10. If it appears that you have too much solvent, you may need to carefully boil off some solvent and repeat step 9.
11. Filter the solution (Büchner) to recover the crystals.
12. Weigh your crystals after recrystallization. (You may have to wait a few days to get a final weight of your unknowns.) Calculate the percent recovery of recrystallized material.

*Disposal: Liquid waste goes into the liquid waste container.  
Solid waste goes into the solid waste container.*

Data entry: You will enter your solubility data from part I before you leave lab. This information will be made available on the course webpage for your lab report.

### The Buchner Funnel

1. Find a piece of filter paper large enough to cover all the holes in the bottom plate, yet not curl up the sides of the funnel. It is placed flat on the plate.
2. Clamp a filter flask to a ring stand. This filter flask, often called a suction flask, is a very heavy-walled flask with a side arm on the neck. A piece of heavy-walled tubing connects this flask to the aspirator
3. Now use rubber stopper or filter adapter to stick the Buchner funnel into the top of the filter flask. The Buchner funnel makes the setup top-heavy and prone to fall over and break. Buchner funnels are expensive!
4. The faucet on the water aspirator should be turned on full blast! This should suck down the filter paper, which you now wet with some cold recrystallization solvent. This will make the paper stick to the plate. You may have to push down on the Buchner funnel a bit to get a good seal between the rubber adapter and the funnel.
5. Swirl and pour the crystals and solvent slowly, directly into the center of the filter paper, as if to build a small mound of product there. Don't flood the funnel by filling it right to the brim.
6. Use a very small amount of the same cold recrystallization solvent and a spatula to remove any crystals left in the flask.
8. Leave the aspirator on and let air pass through the crystals to help them dry.
7. It is a good idea to break the seal between funnel and flask before turning off the water. Otherwise water from the faucet will be sucked back into the flask.



Positioning filter paper  
in Buchner or Hirsch funnel

Checklist for completing the "Prelab" section: (refer to Laboratory Syllabus for complete directions)

\_\_\_ Read through the appropriate section of the syllabus.

\_\_\_ *Title.*

\_\_\_ *Purpose.*

*Physical constants.* Create a table of physical constants and safety data for the following compounds.

You do not need solubility data this week:

\_\_\_ acetanilide

\_\_\_ cinnamic acid (trans-cinnamic acid)

\_\_\_ 2-methoxy naphthalene (see experiment 1)

\_\_\_ 2-naphthol (see experiment 1)

\_\_\_ sodium benzoate

\_\_\_ water

\_\_\_ ethanol

\_\_\_ hexane (see experiment 1)

\_\_\_ References

*Structures and equations.*

\_\_\_ Predict your percent recovery from the recrystallization process.

\_\_\_ *Flowchart.* Refer to "Procedure"

\_\_\_ *Calculations.*

Predict the solubility of the 5 benzene derivative in water, ethanol and hexane. Fill in the table.

	Water	Ethanol	Hexane
acetanilide			
cinnamic acid			
2-methoxy naphthalene			
2-naphthol			
sodium benzoate			

code: vs = very soluble

so = soluble

ss = slightly soluble

in = insoluble

**Safety Question:** While you are “swinging” your test tube to dissolve 2-naphthol in ethanol it inadvertently swings out of your fingers and smashes on the floor. What should you do while waiting for the ever-watchful lab assistant to come to your aid?

**Experimental Observations and Data: Experiment #3**

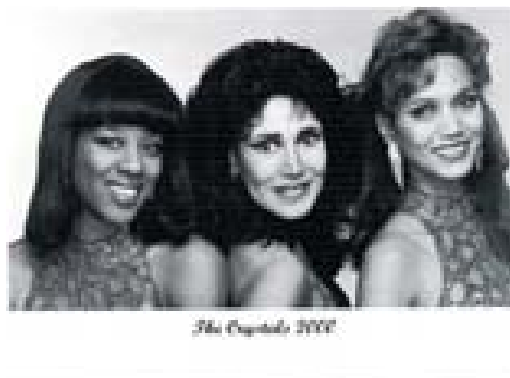
Hand in a copy of your experimental observations and data before you leave lab.

*Experimental Observations.*

- \_\_\_ Who were your partners?
- \_\_\_ What do the solvents and standard solids look like?
- \_\_\_ What did the various precipitates look like?
- \_\_\_ Compare the appearance of the standard solids before and after recrystallization.
- \_\_\_ How did you decide which solvents to use with your unknowns?
- \_\_\_ How readily did your unknowns dissolve/precipitate?
- \_\_\_ Compare the appearance of your unknown solids before and after recrystallization.
- \_\_\_ Any blunders to report?
- \_\_\_ Did you record interesting sights and smells?

*Data:*

- \_\_\_ What was the temperature of the room?
- \_\_\_ What was the temperature of the hot water bath?
- \_\_\_ What was the temperature of the ice bath?
  
- \_\_\_ Observed solubility of each of the 5 standard compounds in: 1) room temperature, 2) hot water, 3) room temperature after hot water and 4) ice bath.
  
- \_\_\_ Observed solubility of your unknowns in various solvents.
- \_\_\_ Record which solvents you used to recrystallize your unknowns.
- \_\_\_ Record the starting weights of your two unknowns.
- \_\_\_ About how much hot solvent did you need to dissolve each unknown?



**Lab Report Checklist:***Results.*

Complete this solubility profile for each standard *compound* from your raw data and shared data:

<i>compound</i>	Room temp 1	Hot Water	Room temp 2	Ice bath
hexane				
ethanol				
water				

code: vs = very soluble, so = soluble, ss = slightly soluble, in = insoluble

\_\_\_ Calculate the percent recovery for the recrystallization of your unknowns.

Mass after recrystallization x 100 / mass before recrystallization = % yield.

Show calculations please.

*Discussion and Conclusion.*

\_\_\_ Compare your experimental solubility data with your predictions. Is the published information on solubility helpful?

	Experimental Water Room Temp 1	Predicted Water Rm Tp 1	Experimental Ethanol	Predicted Ethanol	Experimental Hexane	Predicted Hexane
acetanilide						
cinnamic acid						
2-methoxy naphthalene						
2-naphthol						
sodium benzoate						

\_\_\_ Compare your experimental solubility data with class data. Be specific.

\_\_\_ Which of the following choices represent advantages of the recrystallization technique?

- Finding an appropriate solvent may be time consuming.
- Large or small quantities of solids may be recrystallized.
- Significant sample loss usually occurs.
- Recrystallization removes impurities.
- Recrystallization only works with solids.

\_\_\_ Why does solubility vary with temperature?

\_\_\_ Compare the experimental % recovery with predicted % recovery (prelab).

\_\_\_ How would you quantitatively measure the solubility of a compound (e.g. 0.15 g/mL)?

\_\_\_ Why do you want to keep the amount of solvent to a minimum for recrystallization (Part II.8)?

\_\_\_ Why did we use vacuum filtration (with a Büchner) instead of gravity filtration in this experiment (Part II.10)?

**Green Question:** Not all solvents are equally environmentally friendly. Rate the three solvents you used in this lab according their friendliness. Explain your reasoning. Might this be a factor in your decision which solvent to use for recrystallization?