Experiment 1 — Recrystallization


**Introduction:**

Recrystallization is an important method for the purification of solids. In this experiment you will be given an impure sample of an unknown organic solid. The object is to purify the solid and identify it by its melting point. The unknown will be one of the compounds listed in the table below. So that you gain some experience working on both macro- and micro-scales, you will carry out the recrystallization with 1 g and then again with 50 mg of material.

Recrystallization involves dissolving a solid in a solvent and crystallizing it again, taking the opportunity to discard impurities along the way. One normally chooses a solvent in which the solubility increases significantly with temperature. The solid is dissolved in a minimal amount of hot solvent, and the solution is filtered to remove *insoluble* impurities (e.g., other compounds, dust, etc). On cooling of the solution, the desired compound crystallizes, leaving *soluble* impurities in solution.

Ideally, one would like to recover the entire desired solid completely free of contaminants. Unfortunately, this is rarely possible. Usually, if most of the material is recovered, it is not very pure, and extremely pure material can be obtained only in low yield. The trick is to find the proper balance between yield and purity.

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**Unknowns** (this table will be posted in lab)

<table>
<thead>
<tr>
<th>Compound</th>
<th>mp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>p</em>-((dimethylamino)benzaldehyde</td>
<td>74</td>
</tr>
<tr>
<td>vanillin</td>
<td>82</td>
</tr>
<tr>
<td>1-naphthol</td>
<td>95</td>
</tr>
<tr>
<td><em>o</em>-toluic acid</td>
<td>107</td>
</tr>
<tr>
<td>acetanilide</td>
<td>114</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>122</td>
</tr>
<tr>
<td>benzamide</td>
<td>129</td>
</tr>
<tr>
<td><em>m</em>-nitrobenzoic acid</td>
<td>141</td>
</tr>
<tr>
<td><em>o</em>-nitrobenzoic acid</td>
<td>147</td>
</tr>
<tr>
<td>salicylic acid</td>
<td>159</td>
</tr>
<tr>
<td><em>o</em>-nitrobenzamide</td>
<td>176</td>
</tr>
<tr>
<td><em>p</em>-anisic acid</td>
<td>183</td>
</tr>
<tr>
<td><em>m</em>-hydroxybenzoic acid</td>
<td>202</td>
</tr>
</tbody>
</table>

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— data taken from the *Aldrich Catalog* or the *Merck Index*
Experiment A — Macroscale recrystallization of an unknown.

Note: Always add a boiling chip before heating any solvent or solution. Never add a solid to a liquid at or near its boiling point.

You will receive about 1 g of your impure unknown. Set aside about 100 mg for use in part B, and weigh the remainder accurately on the top-loading balance. When you have time, you'll need to measure the mp of the impure material; don't do it now — you need to get started on the recrystallization! Place your weighed sample in a 125-ml Erlenmeyer flask and add a boiling chip. Heat about 150 ml of water to boiling in a separate flask (+ boiling chip!) using a hot plate.

Now, dissolve the solid in a minimal amount of boiling water. This is done by adding the solvent to the solute (not the other way around!) in small increments and bringing the solution to a boil. Start out with about 10 ml of water and add a few ml at a time until all the soluble stuff dissolves. (Don't measure it out, just estimate!) Watch how much solid dissolves each time — this will give you an idea how much water you'll need to add to dissolve it all. Just be careful not to add too much water, or you'll have to reduce the volume later. Keep in mind that some insoluble material within your sample will not be soluble in water and addition of extra solvent will not help. Record the amount of water that you used and determine what is the ratio between solid and solvent that is needed.

All the unknowns used in this experiment should be colorless. If your solution is colored at this point, the color is due to an impurity. Small amounts of highly colored compounds are common and pesky contaminants. These are often polar or highly conjugated aromatic compounds, and usually adsorb ("stick") strongly to charcoal (an amorphous form of carbon similar to graphite). Adding charcoal at this stage is usually the best way to completely remove such contaminants.

Allow the boiling solution to cool slightly, and add a small amount (about 10 mg) of charcoal. (Note: not "10,000 mg" — OK, you may want to use a balance the first time to get a rough idea what 10 mg looks like; the point is, don't waste time weighing it accurately, just scoop up a bit and chuck it in!) Do not add charcoal to a boiling solution, as this will likely cause a boil-over. You don't need to cool it all the way down to room temp, just to about 10 °C below boiling. If you're not sure if it's cool enough, carefully toss in a bit and see if the solution starts foaming or bubbling.

Again heat the solution to boiling, then filter it by gravity through a pre-warmed funnel containing fluted filter paper. The solution must remain hot during this operation. This is important — if you heat the solution, then remove it from the hot plate and try to do the filtration on the benchtop, everything's going to cool down, right? Solid will precipitate all over the place and make a terrible mess. The trick is to keep everything hot during the filtration! Rinse the paper with a little hot solvent to dissolve any crystals that may have formed.

Slow crystallization is the key to getting high purity product. Plunging the hot solution into ice may cause tiny crystallites to crash out of solution (if it doesn't break the flask), and lots of impurities will end up trapped in the crystal lattice. Instead, allow the filtrate to cool slowly. (editor's note: This would be a good place to stop between periods.) After the cooled solution has stood for about 30 minutes, crystals should form. If no crystals have formed, try scratching the flask with a glass stirring rod below the solution level — the scratches and glass chips may provide nucleation sites for crystal formation. If this doesn't work, try adding a tiny seed crystal (from your original solid sample) to get things started Once crystal formation has stopped, cool the flask in ice to complete the crystallization. Collect the crystals by suction filtration using a Büchner funnel. Wash the crystals with a few milliliters of cold water, and press them down with a clean spatula.

Dry the crystals for at least a day on a tared watch glass or filter paper. Weigh the crystals; determine their melting point (record the melting range accurately). This should establish the identity of your unknown. Just to be sure, you may want to check that the known data are consistent with the compound's observed behavior (e.g., if you have identified your water-soluble white solid as a compound that is known to be an insoluble red solid, you have a problem). Also, be sure to report the structure of your unknown! (as always)

Report the total weight of the pure compound, and calculate the percent recovery. Place your product in one of the bags provided, label it properly, and turn it in. (Instructions for labelling products can be found in the syllabus; Do not attach the sample to your report!!!) Your sample will be checked for appearance, mass, and melting point, so try not to dump it on the floor.
Experiment B. Microscale recrystallization of an unknown.

Recrystallize about 50 mg (record the actual mass accurately) of your impure solid using the Craig tube technique.

Figure 1. Microscale recrystallization using a Craig tube.

Use a similar ratio between compound and water to what you have used in the large-scale experiment. Heat the mixture in a sand bath or in a beaker of boiling water (this will get it very close to boiling). If you want to use a sand bath, keep in mind that it's sometimes difficult to control the temperature — make sure you have the temperature stabilized first, and make sure you don't point your tube at anyone as you (carefully) stick it in the hot sand. (A sand bath is necessary for heating things at higher temperatures; but in a research lab, one would probably use an oil bath instead of a sand bath.) A better method for this experiment is to heat your test tube in a beaker of boiling water. Filter the solution using hot pipet-filtration method or Hirsch funnel as demonstrated in the video.

Once again, report the total weight of pure solid obtained, the percent recovery, and the melting point (range!). Turn in your product properly labelled. (Don't combine it with the material from part A!)

Things to think about before lab (no, you don't have to answer these questions in your pre-lab write-up, but definitely think about them before coming to lab.)

i. Why add boiling water in small portions? Why not just dump in a lot right away?

ii. How would the melting point of your product be affected by impurities?

iii. Given your answer to part ii, if your melting point were 118 °C would your compound more likely be acetanilide or benzoic acid? Are there any other possibilities? What if you had been really sloppy with the crystallization?

iv. One could increase the yield by allowing some or all of the solvent to evaporate before the final filtration. Is this a good idea? Explain.

v. The first filtration is done by gravity and the second by suction. Why? What would happen in the hot filtration were done by suction? What would happen if the crystals were isolated by gravity filtration? (This may be a tough one to answer until you've actually gone through it once in lab.)

vi. Suppose your unknown is p-(dimethylamino)benzaldehyde. As you try to dissolve it in boiling water, the solid disappears and you see what looks like drops of oil on the bottom of the flask. What happened? What should you do now?
Also consider/work through the following situations/problems. The *Merck Index* is a good place to look up the necessary solubility data.

1. If you have not done so already, look up your unknown (which is now presumably known) in the *Aldrich Catalog*, *Merck Index*, and *CRC Handbook*. List the reported melting range (this will probably differ slightly from one source to another — why?), solubility data, and toxicity information.

2. Based on the reported solubility data for your "unknown", what other solvent(s) might be used for the recrystallization? Which solvent(s) would definitely work, and which might require solubility tests to determine whether they could be used? In general, what criteria would you use to deciding whether a solvent will work well for a recrystallization?

3. (a) Water is a good solvent for recrystallizing benzoic acid or benzamide, but not for recrystallizing sodium benzoate. Why does it work well for the first two and not for the third?

   (b) Suggest an alternative solvent that might be used to recrystallize sodium benzoate.

   (c) An alternative to using a single solvent is to use a mixed solvent system with two different solvents. Briefly outline a procedure for recrystallizing sodium benzoate by such a method.

4. Water/methanol and water/acetone are viable mixed solvent systems for recrystallizations, but water/chloroform and water/pentane are not. Explain.

5. Suppose that after preparing about 20 g of benzanilide you found that your solid product was contaminated with aniline and benzoic acid (about 5 - 10% of each), and it was green. Outline a procedure for isolating the pure product by recrystallization.