

Recrystallization

Recrystallization is a very common technique used to purify solids. A material termed *impure* is a mixture of two or more components, from which only one component is desired. The other materials are the *impurities*. Thus, recrystallization and other methods of purification are methods of *separation*.

Besides purifications, there are also separations in which all of the components of the mixture are desired and must be separated from each other. Many experiments this semester involve a separation method.

There are two different scale or size recrystallization procedures in this experiment. Each person will do one size of recrystallization, data will be shared. Each person will analyze and compare both methods.

PRE-EXPERIMENT ASSIGNMENT

Study this chapter of the manual and the lecture notes on the Chemistry Department web site. Do the first six parts of your notebook write-up. Write a procedure for both scale reactions. You will not know which one to carry out until class time.

A student who has prepared for the Recrystallization experiment should be able to:

1. Identify the purpose of recrystallization (the purification of solid samples).
2. Identify desirable properties of recrystallization solvents (does not dissolve the compound to be purified when cold, does dissolve the compound when hot, has a relatively low boiling point for easy removal from the purified compound by evaporation, and does not react with the compound being purified).
3. Describe recrystallization briefly. Also, identify the steps in the recrystallization process and the reasons for them. The seven steps are:
 - Choosing a solvent
 - Adding hot solvent until the compound dissolves
 - Adding decolorizing charcoal (if colored impurities are present)
 - Filtering the resulting solution while it is still hot (if insoluble impurities present)
 - Cooling the solution and obtaining crystals
 - Suction filtration to isolate the compound
 - Drying the crystals
4. Draw the setup used for, and identify components from a drawing of, the setups used for suction filtration. Also, explain the function of the components of the apparatus.
5. Recognize and explain the behavior of samples when they are melted, including both pure and impure samples. Note: Impure samples may contain either soluble or insoluble impurities. (This is a review item from the first experiment, important here.)

6. Draw the structure given the name, or give the name from the structure, of the compounds used in the day's experiment, and give the role of each (reactant, solvent, catalyst, etc.).
7. Identify and explain safety considerations for the day's experiment.
8. Perform the day's experiment safely and successfully.

Quizzes given after the experiment has been performed may also include:

9. Calculate the percent recovery from a recrystallization experiment, given sufficient data.
10. Predict the effects of procedure changes and errors during the recrystallization process, including the use of too much and too little solvent, as well as the effects of cooling rate in the crystallization step.

Safety Precautions

You will be heating an extremely flammable liquid (ethanol). Have no open flames in the lab. Ensure a boiling stone or boiling stick is in the vessel prior to heating. If you forgot to add the boiling stick or stone, remove the vessel from the hot water, allow to cool, add the boiling stick or stone, then return to the hot water.

The test tube or reaction tube will contain very hot liquid. Handle with care. Hot glass looks cool. Use a test tube clamp, a three prong clamp, or a paper towel to handle the hot tubes.

Do not look down the mouth or barrel of a heated test tube.

Benzoin is approved by the FDA as an artificial bitter almond flavoring for foods^{i,ii}. Benzoin in the solid and concentrated form is irritating to the skin and eyes.ⁱⁱⁱ Do not ingest or breathe this compound. Wash your hands after finishing the experiment.

You will be using a Mel-Temp apparatus. The safety procedure dealing with a Mel-Temp are the same as those covered last week. Do not put a room-temperature thermometer into a hot Mel-Temp. Never cool a hot thermometer by running cold water over it or by placing it in an ice bath. Do not place a hot thermometer on a cold bench top. It will often shatter, if you do any of these things. It also does not help to remove the thermometer and wave it around; the Mel-Temp apparatus takes longer to cool.

Do not leave a Mel-Temp on when you are not actually using it. Do not leave one running unattended. Do not heat it beyond the capacity of the thermometer (210°C). Do not touch either the hot metal block of the Mel-Temp or the hot (blue) end of your thermometer.

Procedures

Your instructor will let you know which size recrystallization you will be performing. When you finish the experiment, exchange your data with another student who carried out the other scale experiment. Compare the results of the two size methods.

Microscale Recrystallization (~60 mg)

Place about 3 inches of tap water and one boiling stone into a 250 mL beaker. Place on a hot plate and turn the setting to about 4. The water should not boil.

Weigh approximately 0.06 g (60 mg) of impure benzoin. Do not waste time measuring exactly 0.0600 g, instead weigh out some amount close to 0.06 and be sure to record all the digits the balance provides. (Reasonable values are 0.05823g, or 0.0639 g. An improper value would be 0.06 g. All of the balances in the lab record to 3 or 4 decimal places.) Some instructors take off for wasting time by getting exact masses (0.0600 g). Record the mass directly in your lab notebook. Do not record the mass on a piece of paper, or simply remember it and then later write the value in your lab book. Points will be deducted for not recording data directly in notebook.

Place the benzoin in a reaction tube. Using a Pasteur pipette, add 20 drops of 95 % ethanol to the reaction tube. Add a boiling stick (usually found in a box labeled 'wooden applicator sticks'). Place in the hot water bath until the ethanol just begins to boil. Stir using the boiling stick. If the solid does not dissolve in the hot ethanol, remove the tube from the hot water, add more ethanol dropwise, return to the hot water. Add just enough solvent until all the solid dissolves. The ethanol must be kept hot during this process, but should not be allowed to boil away. Ethanol boils at 78°C and water boils at 100°C. The ethanol will begin to boil before the water boils.

As soon as all the solid has dissolved, remove tube from water bath. Turn hot plate off and unplug. Allow tube to cool to room temperature undisturbed. It is important for the solution to cool slowly. Place the tube in a 50 mL beaker and surround it with Kim-Wipes as insulation to slow the rate of cooling. Allow to cool to room temperature. Crystals should form during this time. If liquid droplets forms instead (this is called oiling out by chemists), try scratching the inside of the tube with a glass stirring rod. If this fails, consult your instructor who might give you additional instructions, or add a seed crystal (a crystal of benzoin from the original bottle) to initiate crystallization. Make an ice-water slurry in a 150 mL beaker. After the tube has reached room temperature, place the tube in the ice bath for a minimum of five minutes.

Squeeze the bulb of a Pasteur pipette to expel air from it. While keeping the bulb squeezed, push the pipette to the bottom of the reaction tube. Keep the tip of the pipette firmly seated in the bottom of the tube and slowly release the pressure on the bulb. This process will draw liquid into the pipette while leaving most of the solid behind.

Weigh a large piece of filter paper. Using the flat blade of your microspatula, scrape the crystals onto the weighed filter paper. Spread the crystals out on one half of the paper and fold the paper over the crystals. Press down on the paper to squeeze out excess liquid. Next, unfold the paper and allow the crystals to dry. When the crystals are dry, determine the mass of the recovered product and the melting point range. At the same time determine the melting point range of some of the unrecrystallized starting material. If the

crystals do not go easily into the capillary, chances are they are not fully dry, and will not give an accurate melting point.

Remember that shrinking or sintering does NOT count as the start of the melting point range. You must start to see an actual change of the substance from solid to liquid. If the melting point range for your recrystallized benzoin indicates that it is impure (is broader than 4° , or is 4° or more from the literature value) dry the crystals some more and retake the melting point SLOWLY. Compare the melting point of the recrystallized benzoin to the literature melting point, which you can find on-line, in a chemical catalog or in the on-line notes on the departmental web page.

Small Scale Recrystallization (~0.4g)

Place about 3 inches of tap water and one boiling stone into a 250 mL beaker. Place on a hot plate and turn the setting to about 4. The water should not boil.

Weigh approximately 0.4 g (400 mg) of impure benzoin. Do not waste time measuring exactly 0.4000 g, instead weigh out some amount close to 0.4 and be sure to record all the digits the balance provides. (Reasonable values are 0.4423g, or 0.3639 g. An improper value would be 0.4 g. All of the balances in the lab record to 3 or 4 decimal places.) Some instructors take off for wasting time by getting exact masses (0.4000 g). Record the mass directly in your lab notebook. Do not record the mass on a piece of paper, or simply remember it and then later write the value in your lab book. Points will be deducted for not writing data directly into notebook.

Place the benzoin in a test tube (not a reaction tube). Add ~4 mL of 95% ethanol to the test tube. Add a boiling stone and heat in a water bath until the ethanol just begins to boil. Shake the tube to mix. If the solid does not dissolve in the hot ethanol, add more ethanol dropwise until all of the solid just dissolves. The ethanol must be kept hot during this process, but should not be allowed to boil away. Ethanol boils at 78°C and water boils at 100°C . The ethanol will begin to boil before the water boils.

As soon as all the solid has dissolved, remove tube from water bath. Turn hot plate off and unplug. Set the tube aside and allow it to cool to room temperature undisturbed. Crystals should form during this time. If liquid droplets form instead (called oil formation by chemists), try scratching the inside of the tube with a glass stirring rod. If this fails, consult your instructor who might give you additional instructions, or add a seed crystal to start crystallization.

Make an ice-water slurry in a 150 mL beaker. After the tube has reached room temperature, place the tube in the ice bath for a minimum of five minutes. While the tube is cooling, set up the filtration apparatus as illustrated in the on-line notes on the organic chemistry web page. There should not be an open path through the funnel. A frit should be in place at the bottom of the funnel as shown in the schematic. If this is missing consult your instructor. The correct filter paper for the Hirsch funnel is 1.5 cm in diameter or about the size of a penny. Use only **one** layer of filter paper on top of the frit. Vacuum

lines are located in both sides of each hood. Be sure to clamp the flask as shown in the figure. Suction filtration assemblies have a tendency to tip over when in use if they are not clamped.

After the crystals have been in the ice bath for five minutes, wet the filter paper on the funnel with ethanol (the solvent used in the recrystallization). Then turn the vacuum on and make sure that the filter paper is pulled down onto the frit. Pour and scrape the crystals and the mother liquor from the test tube onto the Hirsch funnel. Scrape out as many of the crystals as possible with the flat blade of your spatula.

Rinse the remaining crystals in the test tube with a few drops of *cold* ethanol and pour it onto the Hirsch funnel. When all of the liquid is gone from the crystals on the funnel, continue to suction for about 5 minutes to help crystals to dry faster.

Carefully break off the vacuum by disconnecting the tubing. Spread the crystals out on a larger piece of filter paper and allow them to air dry. When they have dried, weigh them and determine their melting point range. At the same time, determine the melting point range of some of the unrecrystallized starting material. If the crystals do not go easily into the capillary, chances are they are not fully dry, and will not give an accurate melting point.

Remember that shrinking or sintering does NOT count as the start of the melting point range. You have to start to see an actual change from a solid to a liquid. If the melting point range for your recrystallized benzoic acid indicates that it is impure (is broader than 4°, or is 4° or more from the literature value), dry the crystals some more and retake the melting point SLOWLY. Compare the melting point of the recrystallized benzoic acid to the literature value.

CLEANUP

Used capillaries and broken ones should be put into the broken glass container. Excess benzoic acid from this experiment should be placed in the non-halogenated solids containers in the hood. Excess ethanol and liquid collected in the bottom of the suction flask, can go down the drain. (Ethanol is biodegradable and sewage treatment plants adequately degrade it.)

Wash all glassware with soap, water and brushes. Return glassware to drawers.

Wipe up work area with sponge. Dispose of all rubbish.

POST-EXPERIMENT ASSIGNMENT

Share your data with a neighbor that carried out the other size experiment. Complete the datasheet and turn in before leaving class. Turn in the white notebook pages from your lab notebook. Staple multiple sheets together. Tear off rough edges.

Prepare for the recrystallization portion of the next quiz. Remember that you may be asked questions on anything you should have learned from assigned readings, pre-experiment lecture, or doing the experiment.

REFERENCES

ⁱ FDA Code of Federal Regulations title 21,

<http://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?FR=172.515>

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ⁱⁱ NIH Benzoin toxicity study [http://ntp.niehs.nih.gov/?objectid=0705EA6F-B605-EF3D-](http://ntp.niehs.nih.gov/?objectid=0705EA6F-B605-EF3D-C83488975B658812)

[C83488975B658812](http://ntp.niehs.nih.gov/?objectid=0705EA6F-B605-EF3D-C83488975B658812) (December 26, 2010)

ⁱⁱⁱ MSDS Benzoin Mallinckrodt Chemicals, <http://www.jtbaker.com/msds/englishhtml/b1428.htm>

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