



Lab #7: GREEN CHEMISTRY

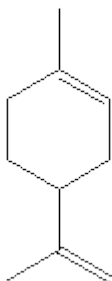
CO₂ extraction--Isolation of Limonene from Orange Rind

OBJECTIVE

To extract the essential oil limonene from orange rind using a green chemistry method.

BACKGROUND

Essential oils are organic compounds that are extracted from natural sources and used in many products such as flavorings, fragrances, and cleaning products. Limonene is the major component of orange oil, which is found in the outer, colored portion of the rinds of oranges and other citrus fruits. The structure of limonene is shown below.



Traditionally essential oils have been extracted through the use of steam distillation or organic solvent extraction. During the past two decades, great strides have been made in technology that uses supercritical or liquid carbon dioxide in place of organic solvents. CO₂ is useful as a 'green' alternative solvent because it provides environmental and safety advantages; it is nonflammable, relatively nontoxic, readily available, and environmentally benign. Although CO₂ is a greenhouse gas, when used as a solvent it is captured from the atmosphere, not generated, resulting in no net environmental harm.

Another major benefit of using CO₂ as a solvent is its accessible phase changes. Unlike other gases, relatively low temperatures and pressures can be used to form liquid and supercritical CO₂. As shown on the phase diagram in Figure 1, CO₂ sublimates (goes directly from solid to gas) at normal atmospheric pressure of ~1atm. The triple point of CO₂, where solid, liquid, and gas phases coexist in equilibrium, is achieved at 5.1atm and -56.6°C. At or near this point, dry ice melts, forming liquid carbon dioxide. If the temperature and pressure are increased to the critical point (72.8atm and 31.0°C), the CO₂ exists as a supercritical fluid and has no distinct liquid or vapor phase, but properties that are similar to both. Dry ice sublimates at atmospheric pressure and temperatures above -78°C. If the CO₂ is sealed in a vessel during sublimation, the internal pressure in the vessel increases. After the temperature and pressure have increased sufficiently, liquid CO₂ forms.

In this experiment, you will use liquid CO₂ to extract the essential oil limonene from orange rind. You may also choose to extract and isolate the essential oil from something other than orange rind. You may, for instance, choose to extract eugenol from cloves or cinnamaldehyde from cinnamon. You may also try lemon peel instead of orange etc. If you do want to be adventurous you may extract the essential oil of any natural product as long as you supply it (spices and fruit peelings work well).

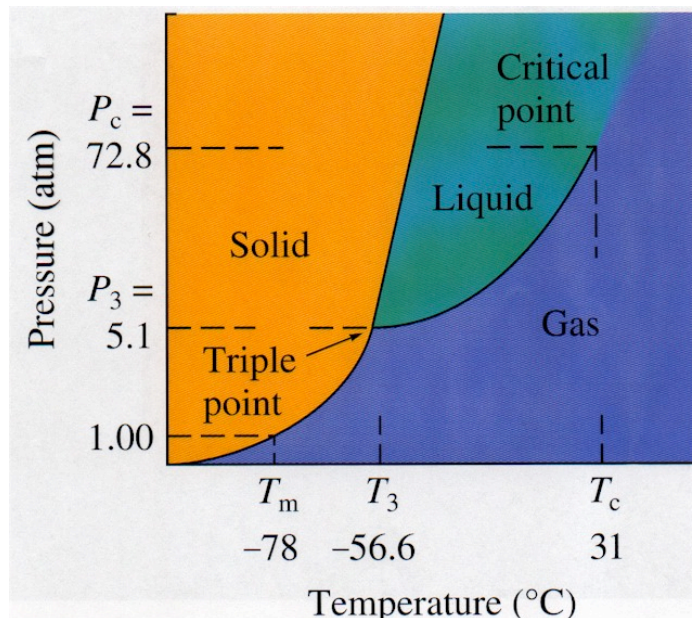


Figure 1: The phase diagram for carbon dioxide.

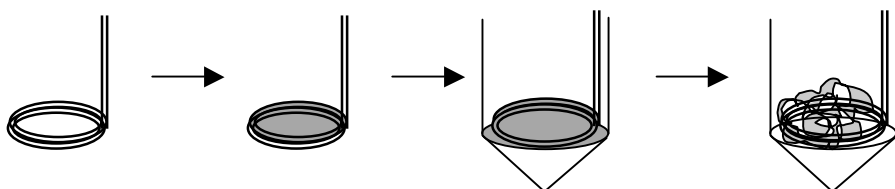
Safety Precautions

Special care is required when the tube is in the water bath because the tube could explode or the lid could fly off due to the high pressure created in the centrifuge tube during the extraction. Use only the equipment and methods mentioned here, and do not, under any circumstance, use glass products as a substitution. It is highly recommended to perform this experiment in the hood.

PROCEDURE

- 1. Preparing the Orange rind (or any substance you bring in).** Grate only the colored part of the peel of 1/2 of a medium-sized orange with the smallest grating surface of a standard cheese grater or zester into a pre-weighed weighing boat. Make sure you have at least 1.5 g of grated orange rind.
- 2. Extraction Vessel:** Record the mass of a 15 mL centrifuge tube. To extract larger sample sizes we have 50 mL conical vials available. Using a 20 cm piece of copper wire and a piece of 1.5 cm filter paper¹, make a solid trap as shown below. Wrap three coils of wire such that the apparatus fits inside the tube with the coils stopping near the beginning of the taper. Use the rest of the wire as a handle projecting up from the coils. All wire should be inside the tube. Cut off any extra wire. Put one piece of filter paper between the coils, making a base to support the solid, and fold up the edges around the wire. Slide the solid trap into tube. Add about 1.5 g of grated orange rind. **Do not pack tightly** as a tight pack may prevent liquid carbon dioxide from freely passing through.

¹ **Note:** If you are extracting a finely powdered spice then it is recommended that you place the spice in an empty tea bag (provided for you) and seal. The tea bag filtration will keep the spice particulates from mixing with your extracted essential oil.



3. Extraction. Fill a **PLASTIC** graduated cylinder two-thirds full with hot tap water (40-45° C) and place it under the hood. Fill the centrifuge tube with finely crushed dry ice, tapping the bottom of the tube on the counter and adding more ice until the tube is full, then cap the centrifuge tube quickly and tighten it until the cap stops twisting. Be careful not to close it too tightly or the tube may explode. Lower the full centrifuge tube tapered end first into the graduated cylinder water bath waiting in the hood. Pull the hood safety glass down as soon as you place the centrifuge tube into the warm water bath. The dry ice should become liquid CO₂ after a minute and remain in the liquid phase for about 3 minutes until all the gas has seeped out the top. If the CO₂ has not entered the liquid phase after 2 minutes, the centrifuge tube did not have a tight enough seal, and either the cap and tube should be replaced, or the dry ice was left in the tube too long without sealing the cap on.

After all the liquid CO₂ is gone, uncap the tube. If necessary, rearrange the solid orange peel before the second extraction. A piece of wire can be used to break up the solid mass and create a channel to the bottom for liquid CO₂. Repeat the extraction by refilling the tube with dry ice, resealing the cap and putting the tube back in the water.

Carefully remove the solid and the trap by pulling the wire handle with tweezers. Pre-weigh a small sample vial before collecting the extracted oil in it, and reweigh the vial after the oil has been collected.

Lab #7 Report Sheet

Name _____

1. Calculate the mass percentage recovery of the oil from the original amount of orange rind used.
2. Write a half page discussion regarding your thoughts about supercritical CO₂ extraction as an example of green chemistry. Find the part of this topic that interests you the most and write about it!