Extraction of Limonene with Liquid CO_2

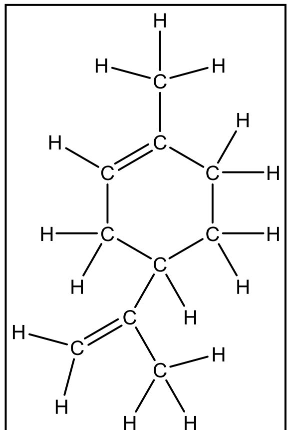
Adapted from McKenzie, Lallie C. et al. "Green chemical processing in the teaching laboratory: a convenient liquid CO_2 extraction of natural products" *Green Chemistry* **2004**, 6, 355-358.

Purpose

- To extract limonene and other essential oils from citrus rinds using liquid CO_2.
- To determine if the amount of limonene extracted from various fruits is statistically different.

Background

Green chemistry, also known as sustainable chemistry, involves designing chemical processes that minimize the use and generation of hazardous chemicals. For many years, essential oils and other chemicals from natural sources were extracted from plants (and animals) using hydrocarbon-based solvents such as hexane, or halogenated solvents like dichloromethane. A substance containing a desirable chemical is ground up and allowed to soak in the hot or boiling solvent for a period of time. The solvent is then evaporated or boiled away, which leaves behind the desired substance or a mixture of substances. Caffeine from coffee beans, fragrances from flowers, and flavor extracts (like limonene) have all been acquired in this way from natural sources. However, many of these solvents exhibit human toxicity, are hazardous for the environment and/or require a lot of energy to produce and evaporate. In addition, because of their environmental and toxicological profiles, it is often very expensive to dispose of waste/used solvents.



Limonene

One substance that has been recently promoted as a green solvent is carbon dioxide. In the small quantities used as a solvent, it poses very few environmental and health risks, and it is cheap and energy-efficient to produce. Liquid CO_2 is a good solvent for limonene ($C_{10}H_{16}$) it is fairly easy to produce from dry ice and because the liquid boils away at room temperature as soon as the extraction vessel is depressurized. Liquid CO_2 extracts limonene very efficiently from citrus rind for another reason, which provides the basis for one of your post-lab questions.

Chemicals and Equipment Needed

2 plastic beakers　　copper wire　　centrifuge tube　　citrus rind　　dry ice

Procedure

1. Using a zester on an orange, lemon or lime, add grated rind to a small piece of paper towel that has been tared on the scale. You need about the size of two pinto beans. Record the mass of the rind. Wrap a wire with a two-inch handle around the paper towel so that you can remove it from the tube later.
2. Record the mass of the empty polypropylene centrifuge tube. Insert the paper towel into the polypropylene centrifuge tube. It should not be so tight that liquid cannot move past the paper. Use a small spatula to press the paper to one side to create a path for liquid CO_2 if necessary.

3. Completely fill the tube with very small pieces of dry ice. Screw the lid on tightly. Place the tube in a *plastic* beaker filled with warm water, 40 – 50 °C, not hot. Cover the plastic beaker with another plastic beaker as a blast shield. Warming the dry ice causes the following phase change, $CO_2(s) \longrightarrow CO_2(g)$. Although liquid CO_2 cannot exist at normal atmospheric pressures, as gas is formed the closed tube causes pressure to build, and liquid will appear, $CO_2(s) \longrightarrow CO_2(\ell)$.

Caution: Any time pressure is created inside a closed container there is the potential for catastrophic depressurization (an explosion). Do not look down at the tube from above. The cap will leak slowly and prevent dangerous pressures from becoming too high.

4. You should see boiling $CO_2(\ell)$ in the bottom of the tube and hear a hiss as $CO_2(g)$ escapes the cap. When the liquid CO_2 has disappeared, remove the cap. *Caution: Do not remove while it is still hissing or you can still see liquid CO_2.*
5. Repeat the liquefaction/extraction process two more times with the same sample of rind. If you stop seeing liquid CO_2, try screwing the cap on tighter, or replacing the vial cap.
6. Remove the paper using the attached wire; you should see a lightly colored oil at the bottom of the centrifuge tube. This essential oil is predominantly D-limonene. Smell it!
7. Record the mass of the tube with the essential oil and determine the amount of essential oil that was extracted from your sample of rind.

Results

Determine the percentage (by mass) of your sample of rind that was D-limonene.

$$Percent\ by\ mass = \frac{mass\ of\ D - limonene\ extracted}{mass\ of\ the\ rind} \times 100\%$$

Record your group's percentage in the appropriate column on the Google document posted on Moodle.

Questions

1. After all of the data from all of the labs has been recorded, determine if there is a difference in the percent D-limonene by mass for the three fruits. Use Excel to calculate the mean, standard deviation, and standard error of the percent D-limonene for the three fruits. Are the differences in the percent D-limonene by mass for the three fruits statistically significant? How do you know?
2. If you are a laboratory technician working for a company in the essential oil industry, which fruit would you utilize to maximize the amount of essential oil extracted per square inch of rind? Assume that all of the fruits are identical in price.
3. What type(s) of intermolecular attractions are present in CO_2?
4. From a molecular perspective (not from a green chemistry perspective), why is liquid CO_2 a good solvent for limonene?
5. Explain how making tea is actually a chemical solvent extraction process.