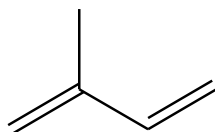


Steam Distillation of an Essential Oil

In this laboratory exercise we will employ Steam Distillation to isolate an Essential Oil from either Mint leaves or Orange rinds. This will involve distilling a mix of the plant material and Water to obtain the Oil, extracting the Oil from the Water, and then isolating the Oil from the extraction solvent. In the end, we will analyze the Oil's composition by separating its constituents using Gas Chromatography.

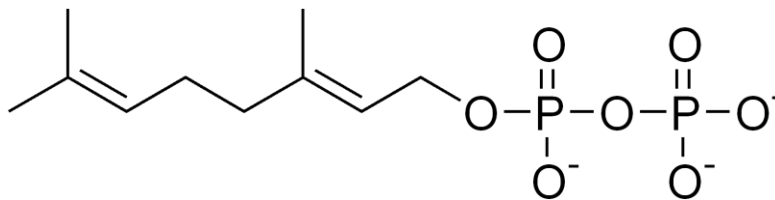
Essential Oils are a mix of fragrant compounds common to a number of plants such as Mint, Lavender, Pine, etc. which are isolated via steam distillation. Because these Oils were once considered to be the essence of the plant, they were initially sought as possible pharmaceuticals and are a part of early medicine's contribution to modern chemistry. Today they are used as flavorings, perfumes and deodorants.

Essential Oils are mixtures of organic compounds that are dominated by the Terpenes and the Terpenoids, oxygen containing derivatives of the terpenes. Terpenes themselves are a class of compounds built on the five carbon skeletal fragment of Isoprene.



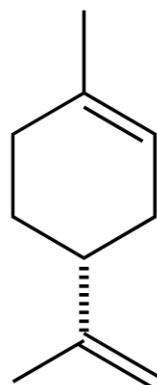
Isoprene

However, most terpenes are biologically synthesized from Geranyl Pyrophosphate, which contains two Isoprene units bound together head-to-tail:

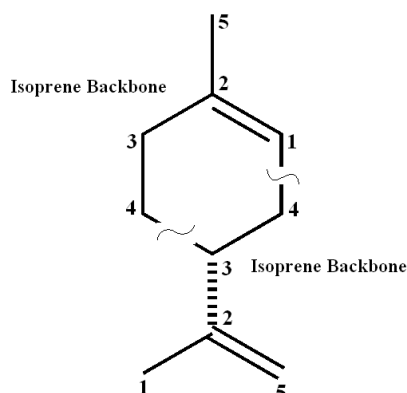


Geranyl Pyrophosphate

So, the carbon backbones of most terpenes contain a multiple of ten Carbon atoms. For example, Limonene, the major constituent of the Oil of Orange has the formula $C_{10}H_{16}$.



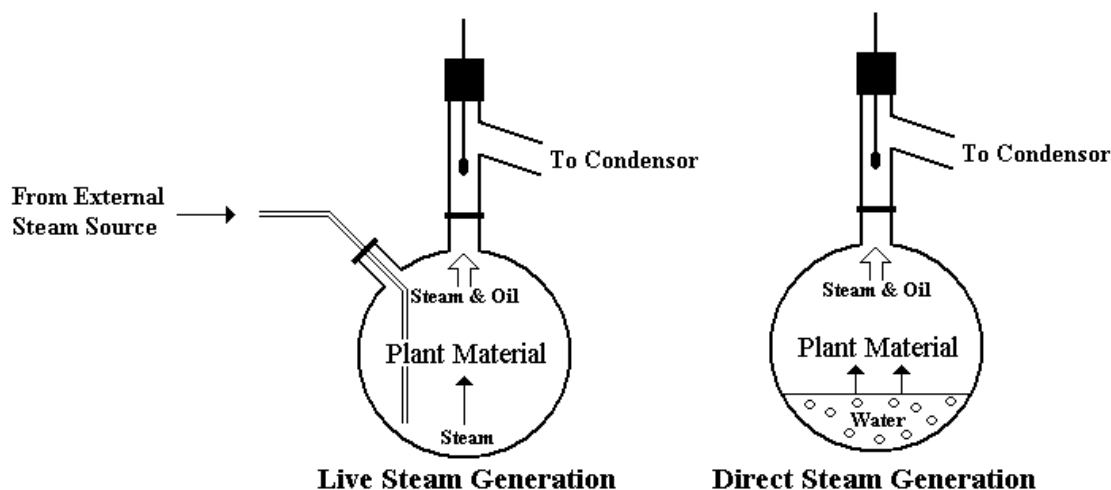
Limonene



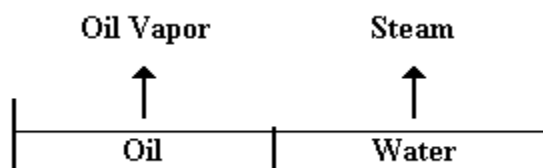
Limonene with Isoprene Units Identified

(Squeeze the rind of an Orange near a lit match and the Limonene released will cause the match's flame to flare as the compound is quite flammable.) The exact composition of these Essential Oils is determined by the plant variety, the plant parts sampled, the time of year the plant is harvested, and the conditions under which the plant is grown.

Attempting to distill these Essential Oils directly from the plant material is generally not feasible. In general, most of the Oils' constituents are high boiling and will decompose under the high heat needed to bring them to a boil. Steam distillation is a much gentler method of achieving the same end. In steam distillation, the distilling pot is infused with steam, which carries the Oil's vapor into the distilling head and then into the condenser, where the Oil and Water co-condense. As an alternative, steam is generated *in situ* in the distilling pot.



Steam distillation works because the Water and the Oil are immiscible. Hence, they boil independent of each other.



So, boiling occurs when the sum of the pure vapor pressures equals the atmospheric pressure:

$$P_{\text{atm}} = P_{\text{Wat}}^{\circ} + P_{\text{Oil}}^{\circ} \quad (\text{Eq. 1})$$

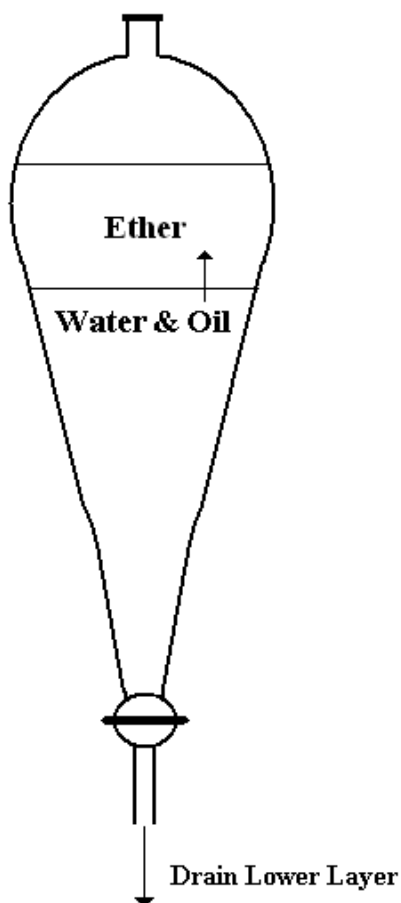
Thus, a mixture of two immiscible liquids boils at a temperature lower than the Normal Boiling Point or either component of the mixture. Because $P_{\text{Wat}}^{\circ} \gg P_{\text{Oil}}^{\circ}$, the mixture will boil at a temperature slightly less than the normal boiling point of Water. This means the Oil will vaporize under very mild conditions.

However, this methodology leaves us with one complication; the distillate is a mixture of Oil and Water. The relative numbers of moles (n) of each component of the distillate will be given by:

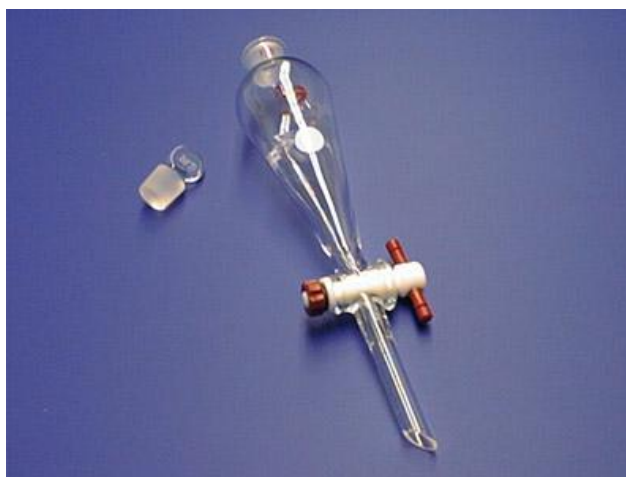
$$n_{\text{Oil}} / n_{\text{Wat}} = P_{\text{Oil}}^{\circ} / P_{\text{Wat}}^{\circ} \quad (\text{Eq. 2})$$

If we know the average molecular weight (M) of the Oil, then we can estimate the mass (m) of Oil that will be obtained in a given amount of Water:

$$m_{\text{Oil}} / m_{\text{Wat}} = (P_{\text{Oil}}^{\circ} M_{\text{Oil}}) / (P_{\text{Wat}}^{\circ} M_{\text{Wat}}) \quad (\text{Eq. 3})$$



We now need to Extract the Essential Oil from the co-distilled Water. We will take advantage of the fact that the Oil is insoluble in Water and is soluble in non-polar solvents like Diethyl Ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$). Ether is added to the Oil-Water mixture in a Separatory Funnel. This funnel allows the two solvents to layer and subsequently we can drain one solvent layer away from the other.



After a few moments of shaking, the Oil will Partition into the Ether layer. Draining the Water layer from the Ether removes the Oil from the Water. The partitioning is almost never complete, so an Extraction is usually carried-out multiple times. The resulting Ether layers are collected and combined. (Caution must be observed when shaking the system. First, the system must be vented continuously because of vapor build-up that occurs within the flask. Second, the shaking cannot be too vigorous or else the system will emulsify. If emulsification occurs, separation of the two layers will become very difficult.)

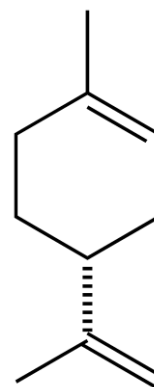
It may seem as though we have traded one problem for another; we now have a mixture of Oil and Ether that must be separated. However, this is not a major problem. The Ether will boil at a low enough temperature that it can simply be boiled off from the Essential Oil. After the Ether is stripped off, our isolation of the Essential Oil is complete.

We will distill one of two Essential Oils; Oil of Orange or Mint Oil.

The Oil of Orange is an Essential Oil derived from the rind of oranges and some other citrus fruits. It is composed of Limonene, α and β Pinene, Myrcene, Octanal, Decanal, δ -3-Carene, and Linalool; with Limonene comprising over 90% of the Oil derived from common orange varieties. Because it is non-polar, Limonene makes a good, environmentally friendly solvent.



http://en.wikipedia.org/wiki/File:OrangeBloss_wb.jpg

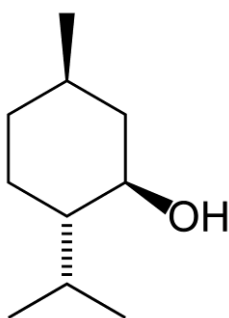
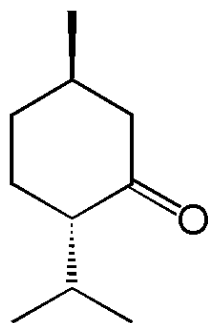
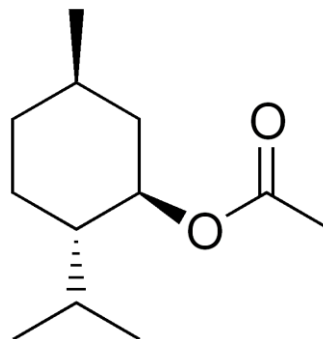
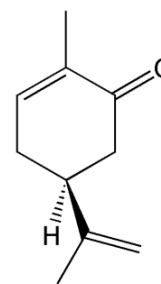


Limonene

http://en.wikipedia.org/wiki/File:Mentha_longifolia_2005.08.02_09.53.56.jpg

Mint Oil is an Essential Oil derived from various mint varieties. The composition of the Oil is dependent on the particular mint variety distilled. For instance, Peppermint's (*Mentha x piperita*) Oil is composed of Menthol, Menthone and Menthyl Acetate. On the other hand, Spearmint's (*Mentha spicata*) Oil is composed of Carvone and Limonene.



**Menthol****Menthone****Menthyl Acetate****Carvone**

In another laboratory exercise we will analyze the Oil obtained using Gas-Liquid Chromatography. By comparing the Gas Chromatographic results with appropriate Standards, we can identify the constituents of the Oil.

Pre-Lab Questions

1. What is the Normal Boiling Point of naturally occurring Limonene? What is the approximate Boiling Point of Limonene during a steam distillation?
2. Quinoline is to be isolated using steam distillation. At 99.6°C the vapor pressure of Water is 750 Torr and that of Quinoline is 10 Torr. If 100 mL of distillate is collected, approximately how many grams of Quinoline will have distilled over?
3. During an Extraction, a solute (S) will partition itself between the two solvent phases with a Partition Coefficient (K) defined as:



$$K = [\text{S}]_2 / [\text{S}]_1$$

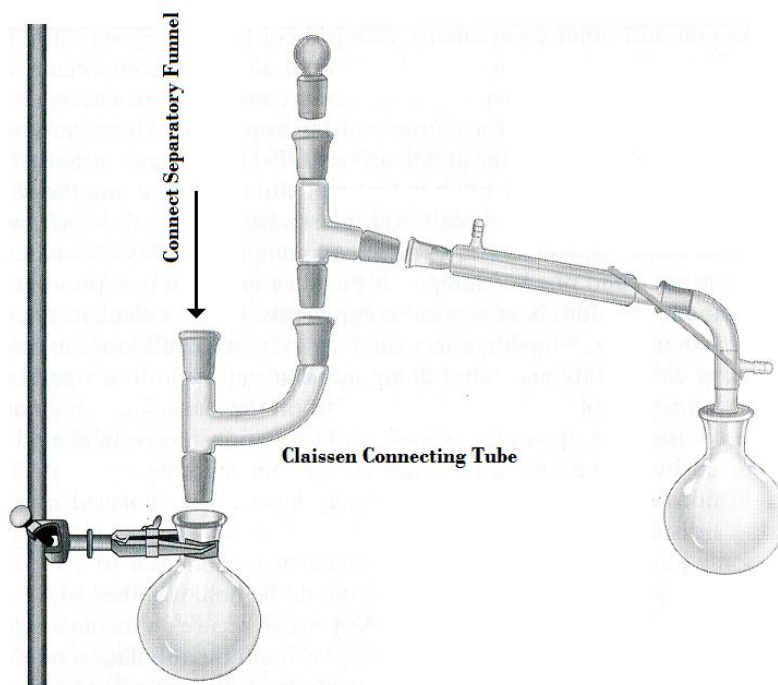
Solute S is found to have a partition coefficient of 15 between Solvent 1 and Solvent 2; with 15 times as much in Solvent 2. Suppose 150 mL of a 0.02M solution of S in Solvent 1 is Extracted with 50 mL of Solvent 2. What fraction of S remains in Solvent 1? If three 50 mL extractions are performed, what fraction of S remains in Solvent 1?

Procedure

Steam Distillation of the Oil of Orange

Week 1

1. Assemble the Distillation apparatus as pictured (roughly) below. Because of the large amount of Orange Ring required, we will use a 500 mL round bottomed flask as the distilling pot. Use a small hot plate as a heat source. We will be generating the Steam directly. Use a 250 mL round bottom flask as a receiver. Use a Claisen connecting tube to connect the distilling pot to the distillation head. Add a Separatory Funnel filled with Water to Claisen tube. This will allow us to easily add Water to the system during the distillation, if needed. Wrap the Claisen in some cotton batting and Aluminum foil to keep it hot during the distillation.



Adapted from:
Operational Organic Chemistry
John W. Lehman

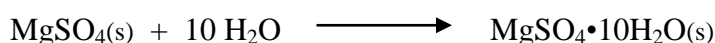
2. Peel three medium Oranges and measure the mass of the peel. Puree the peel with a minimum of Water in a blender. Add the puree to the distilling pot, a 500 mL round bottom flask, using a wide-mouth funnel and a stirring rod. Add enough Water so that the distilling pot is about 2/3 full. Add a boiling chip. Turn on the condenser Water and seal the distilling pot.
3. Begin heating the system slowly. Adjust the heat so that the distilling rate equals about 20 drops per minute. As the mixture boils and distills, you will be losing Water from the distillation mixture. As the level drops in the flask, add small volumes of Water via the

separatory funnel. It is important to watch the Water level because of the high concentration of Sugar in oranges. If the Water level gets too low, the Sugar will caramelize and burn. Also, it is better to add small amounts of Water so that the temperature doesn't drop drastically. Keep the heat at a low, steady level.

4. Collect about 150 mL of distillate. The presence of the Oil in the condensate will cause the drops forming in the condenser to be cloudy. Thus, you can estimate when the condensate no longer contains Oil by noting the absence a cloudy appearance.
5. Transfer the distillate to a stoppered Erlenmeyer Flask. Store the distillate in your drawer until the next lab period.

Week 2

6. Transfer your distillate to a 250 mL Separatory Funnel. Add 20 mL of Diethyl Ether and Extract the Oil. Your laboratory instructor will demonstrate the correct use of the Separatory Funnel. (Do not begin this process until you have been given the appropriate instructions by your lab instructor.) **There must be no flame sources or hot plates on during the use of Ether. Ether is very, very flammable.**
7. Drain the Water layer off into a 250 mL Erlenmeyer Flask. Drain the Ether layer into a small collection flask.
8. Repeat the extraction once more and collect all the Ether fractions in the same Flask.
9. Dry the Ether with a little Anhydrous Sodium Sulfate. This is required because trace amounts of Water will dissolve in the Ether. The Anhydrous Sodium Sulfate will absorb the Water and produce solid Magnesium Sulfate Decahydrate:



Allow the system to dry for 10 - 15 minutes.

10. Decant the liquid into a small beaker. Add a toothpick to the beaker. (This will act as a nucleation site during the boiling.) Place the beaker on a steam bath **in the fume hood**. Boil off all the Ether.
11. Transfer your Oil to a massed and labeled 4-dram vial. Determine the mass of the Oil. Calculate the percentage Oil in the Orange Peel.
12. Save your Oil for further analysis via Gas Chromatography.

Steam Distillation of Mint Oil

Week 1

1. Assemble the Distillation apparatus as pictured below. Because of the large amount of Mint required, we will use a modified Paint Can as a distilling pot. Use a small hot plat as a heat source. We will be generating the Steam directly. Use a 250 mL round bottom flask as a receiver.

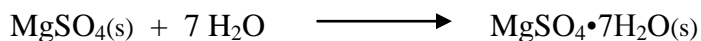


2. Add about one pound of Mint and 400 mL Distilled Water to the "distilling pot". (The Mint should be rather loosely situated in the pot.)
3. Seal the "distilling pot". Begin heating the system slowly. Adjust the heat so that the distilling rate equals about 20 drops per minute.
4. Collect about 150-200 mL of distillate. The presence of the Oil in the condensate will cause the drops forming in the condenser to be cloudy. Thus, you can estimate when the condensate no longer contains Oil by noting the absence a cloudy appearance.

5. Transfer the distillate to a stoppered Erlenmeyer Flask. Store the distillate in your drawer until the next lab period.

Week 2

6. Transfer your distillate to a 250 mL Separatory Funnel. Add 50 mL of Methylene Chloride and Extract the Mint Oil. Your laboratory instructor will demonstrate the correct use of the Separatory Funnel. (Do not begin this process until you have been given the appropriate instructions by your lab instructor.)
7. Drain the Methylene Chloride layer off into a 250 mL Erlenmeyer Flask.
8. Repeat the extraction twice more and collect all the Methylene Chloride fractions in the same Flask.
9. Dry the Methylene Chloride with a little Anhydrous Magnesium Sulfate. This is required because trace amounts of Water will dissolve in the Methylene Chloride. The Anhydrous Magnesium Sulfate will absorb the Water and produce solid Magnesium Sulfate Heptahydrate:

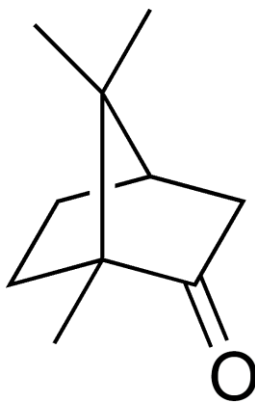


Allow the system to dry for 10 - 15 minutes.

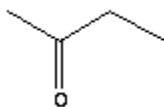
10. Decant the liquid into a 250 mL round bottomed flask. Use a Rotovap to strip off the Methylene Chloride from the Mint Oil. (Your laboratory instructor will demonstrate the use of the Rotovap.)
11. Transfer your Mint Oil to a labeled 4-dram vial.
12. Save your Mint Oil for further analysis via Gas Chromatography.

Post Lab Questions

- The condensate from a steam distillation contains 10g of compound A and 18g of Water. At the temperature of the distillation, the vapor pressure of Water is 660 Torr. What is the approximate Molecular Weight of A?
- Consider Oil of Turpentine.
 - What is the source of this Oil?
 - What are the major constituents of this Oil? (two)
 - Identify the Isoprene backbones in each constituent of this Oil.
 - What was the original source of this Oil?
- In 1800, on the eve of Fredrich Wohler's experiments leading to overthrow of Vitalism, Camphor was one of the few organic compounds known.



- What is the natural source of Camphor?
- Identify the Isoprene backbones in this molecule.
- Provide the IUPAC name for this compound. (Hint: Ketone functionalities are given an -one ending. Thus, the following ketone:



is given the IUPAC name butan-2-one.)