

OFF[®] from Oranges??

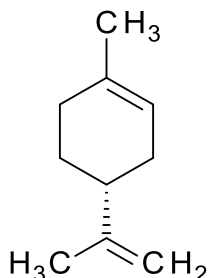
Learning Objectives:

- Extraction of organic compound(s) from natural sources
- Isolation using physical and chemical means
- Identification and quantitation of primary components – yield and purity
- Discussion of green chemistry and what a green manufacturing process is

The Problem

SC Johnson, makers of OFF[®], is looking to prepare a brand-new “green” insect repellent. The scientists at SC Johnson found a “natural” insect repellent that is available right here in the USA. This natural compound is called limonene and is a chemical substance made by citrus fruits. It is a natural protectant against insects. The problem is, “Which peel is better to use, oranges or lemons?” and “What is the best technique for extracting the limonene?”

(D)-Limonene (4R)-isopropenyl-1-methylcyclohexene

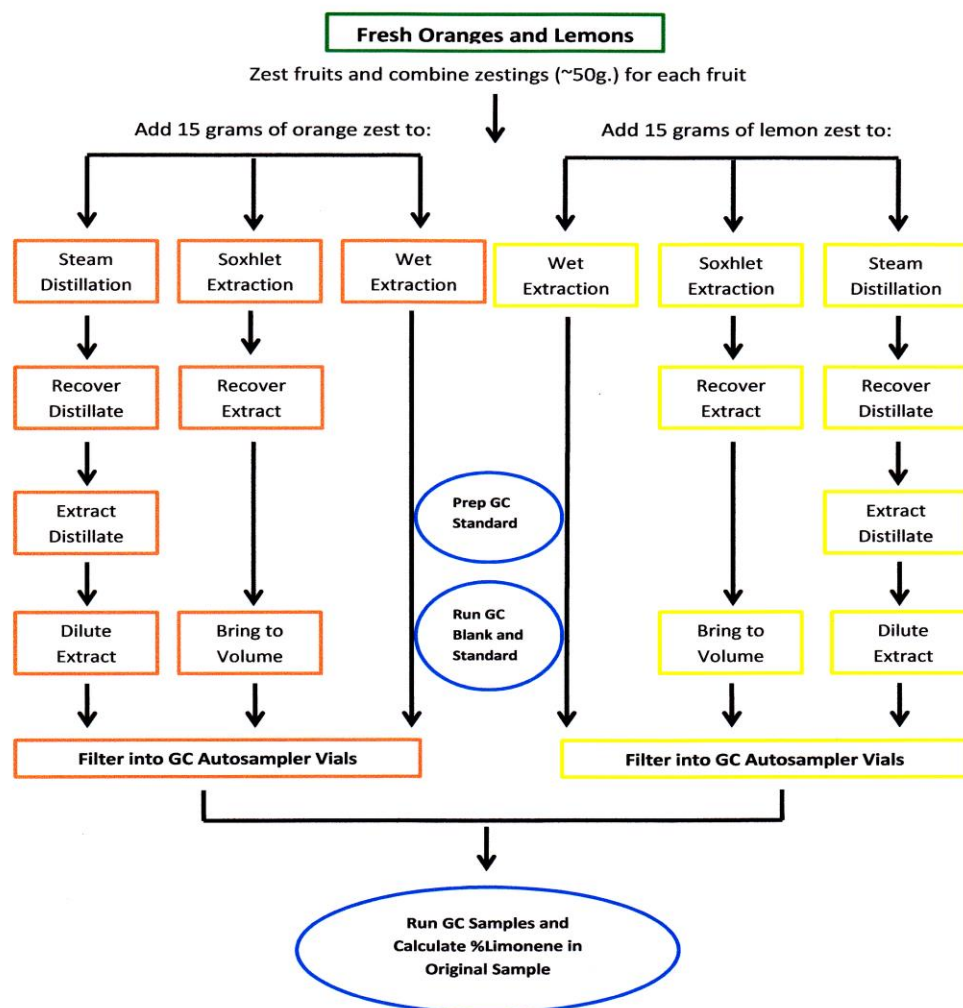


Molecular Formula = C₁₀ H₁₆

Molecular Mass = 136.23 Boiling Point = 176 °C

Basic Analytical Scheme

Limonene Extraction/Analysis – Analytical Scheme



Experimental Procedures:

Zest Preparation :

- Carefully push the fruit against the grater and slide it along its length.
- You should grate until a “scrape” is observed; the bright shiny color has been removed and there is a lighter, dull area remaining.
- Keep rotating the fruit and adjusting the position so that only fresh skin is zested. Do not go back over previously zested areas or too much skin will be removed.



- Tare the plastic weighing boat on the balance.
- Periodically collect the zests from the aluminum pans using the scoopulas to scrape it up.
- Add the zest to the boat until there is approximately **15±0.1 grams of zest for their respective analysis.**
- **Record the weight of zest** on their data sheet.

Turn on the circulating bath to cool all condensers, which are connected in series.

Soxhlet Extraction Teams:

- Place the paper thimble on the balance and press the tare button.
- Using a metal scoop, transfer the zest into the paper thimble, gently packing it down lightly. Record the weight on your data sheet.
- Put some glass wool on top of the zest to keep the small particles in place.
- Remove the extractor body from the condenser and place the thimble inside.
- Add 2 Teflon boiling chips to the round bottom flask. and reconnect to extractor.
- Using a 100mL graduated cylinder, measure and add 175mL of isopropyl acetate to the round bottom flask.
- Carefully reconnect the flask, extractor body and condenser.
- Turn on the rheostat and turn the dial 80 to 90, maintaining a consistent boil.
- Watch the extraction process. Take mental notes on the clarity and color of the solution as the extraction progresses.
- After approximately 30 - 40 minutes (*the instructor will let you know*), turn off the power.
- Disconnect the round bottom flask from the extractor and lower it down into a crystallization dish containing some cold water.
- After it has cooled, transfer the contents of the flask and the extractor into a 200mL volumetric flask with the aid of a glass funnel.
- Bring up to the mark by slowly adding isopropyl acetate using the squirt bottle. Mix.
- Transfer about 1mL to a GC autosampler vial, filtering the sample with the "syringeless" filter. (*sometimes this takes two sets of hands*). Label the vial.
- With the help of the instructor, put your sample into the GC autosampler.

CLEAN-UP (*may be performed by instructors*)

- Remove the round bottomed flask from the extractor body.
- Rinse the flask by adding about 20mL of acetone and swirling the flask.
- Dump acetone into an approved waste collection container.
- When the flask looks clean, go to the sink, rinse it with water and put the flask on the drying rack.

Steam Distillation Teams:

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- Tare a plastic weighing boat on the balance.
- Weigh the zest into the weighing boat and record the weight on your data sheet.
- Add the zest to the 250mL. round bottom flask.
- Using a 100mL. graduated cylinder, add 100mL. of DI water to the zest.
- **Add 2 boiling chips and 3 drops of Antifoam B to the liquid in the flask.**
- Mix the contents by gently swirling the flask.
- Reconnect the flask and raise the mini-jack and heating mantle.
- Place a 50mL screw cap culture tube (the one with the water level mark) under the receiver end of the distillation apparatus.
- Turn on the heating controller. (temperature settings are above)
- It is usually easiest to keep the tube in the 200mL beaker to help hold it steady.
- Collect approximately 35mL. of distillate (approximately up the mark). Cap and label the vial. Carefully put the other vial under the receiver and collect another 10mL. or so. (*observe whether oil is still distilling over. Does the second distillate sample smell of citrus? – Note – this sample will NOT be analyzed*)
- In a fume hood, use a 10 mL graduated pipette to add 10 mL of isopropyl acetate to the distillate/oil mixture.
- Cap the vial and grasping it firmly, mix by inverting and gently swirling the container. You should see tiny oil droplets mixing with the water. After 2 minutes, set the container down in a test tube holder and allow the layers to separate.
- Fill a 10mL. volumetric flask about half full with isopropyl acetate.
- Using a 1mL. automatic pipette, **carefully** transfer 1mL. of the upper (solvent) phase from the vial into the volumetric flask. **Note – it helps if the instructor holds the lower end of the pipette to assure it is submerged in the solvent layer but not allowed to penetrate or suck up the water layer.** Dilute to the mark with isopropyl acetate and mix by inverting several times.
- Transfer about 1mL to a GC autosampler vial, filtering the sample with the “syringeless” filter. (*sometimes this takes two sets of hands*). Label the vial.
- With the help of the instructor, put your sample into the GC autosampler.

CLEAN-UP (*may be done by the instructors*)

- When the round bottomed flask is room temperature, loosen the clamp and remove it from the distilling head.
- The contents can go down the drain and the flask can be washed in the sink with normal cleanser and water.

“Manual” Solvent Extraction:

This simple sample preparation can be prepared by whichever extraction team has gotten their setup extracting first and needs something to fill their time.

- Tare a plastic weighing boat on the balance.



- Weigh the zest into the weighing boat and record the weight on your data sheet.
- Add the zest to the 250mL. Erlenmeyer flask round and record the weight on your data sheet.
- Using a 100mL. graduated cylinder, add 100mL. of isopropyl acetate to the zest.
- Stopper the flask and periodically swirl the contents to extract.
- Transfer about 1mL to a GC autosampler vial, filtering the sample with the "syringeless" filter. (*sometimes this takes two sets of hands*). Label the vial.
- With the help of the instructor, put your sample into the GC autosampler.

Instrumental Analysis Section:

GC "blank" – isopropyl acetate (same as used in extractions)

Quantitative Standard: Fill a 10mL volumetric flask approximately half full with isopropyl acetate. Using a 10 μ L - 100 μ L autopipettor, add 100 μ L of limonene to the flask and dilute to volume with isopropyl acetate. This will make a standard that is 8.40mg/mL

$$\frac{(100\mu\text{L})(0.840 \text{ mg}/\mu\text{L})}{10\text{mL}} = 8.40 \text{ mg/mL}$$



Limonene Extraction from Citrus Peels -Data Sheet-

Analysts Names _____

Date _____

Fruit Analyzed _____

Mass of Zest Used (grams) _____

Extraction Technique _____

Amount of Limonene in Extract (mg/mL) _____ (by GC)

Total Limonene from Sample (grams)

$$\frac{(\text{Amount in Extract mg/mL}) \times (\text{total volume of solvent})}{(1000\text{mg/gram})} = \text{_____ grams}$$

Volume = 100mL for steam distillation and manual extraction techniques

Volume = 200mL for soxhlet extraction technique

$$\text{Yield from Zest (weight \%)} = \frac{(\text{total grams})}{(\text{mass of zest})} \times 100 = \text{_____ \%}$$

Purity of Limonene (% from GC chromatogram area %) _____ %

Bonus Question: Do you prefer orange juice or lemonade? _____

Knock Knock

Who's there?

Orange

Orange who?



Orange you glad you did this experiment?!!!!!!