Introduction:

In this experiment, (+)-carvone will be isolated from caraway-seed oil and (-)-carvone from spearmint oil using preparative gas chromatography (GC). In normal “analytical” GC, very narrow bore (0.25 mm) capillary columns are used which can only accept micro- or nanogram quantities of compounds before “overloading,” in which peaks are huge and broad and poor separation is obtained. In preparative GC, larger bore columns (6 mm) are used and milligram quantities of sample can be injected and separated and the separated peaks condensed and collected to give a few milligrams of each component. Repeated injections of ~10 mg each and combining the fractions collected will provide the 20 or so mg needed for an NMR. Preparative GC is similar to running a very high-quality fractional distillation on small quantities of liquid mixtures.

The odors of the (+) and (-)-carvone optical isomers are distinctly different from each other. The presence of one or the other of these isomers is responsible for the characteristic odors of each of the two oils. The difference in their odors is to be expected, since the odor receptors in the nose are chiral. Although we should expect the optical rotations of the isomers to be of opposite sign, the other physical properties such as boiling point, IR, NMR, refractive indices, and gas chromatography retention time should be identical.

Caraway oil contains mainly (+)-carvone and limonene, and these can be easily separated by gas chromatography. Spearmint oil contains mainly (-)-carvone with a smaller amount of limonene. The (+) and (-) carvones can easily be separated on the preparative gas chromatography column, but the limonene may contain some additional terpenes.

Prelaboratory Exercise:

Explain briefly why limonene, rather than carvone, will elute first from the gas chromatograph.

Cautions:
Avoid contact with (\(+\)-carvone). Surprisingly, this compound is quite toxic. (Maybe that's why some of us don't like caraway seeds!?)

Preparation:

The preparative gas chromatograph (GC\#4, a Varian 920 gas chromatograph with a thermal conductivity detector) must be warmed up for 4 hours prior to doing the separation. Tell the instrument room operator to help you turn it on. Be sure that helium gas is flowing before turning on the GC.

Pure spearmint oil and pure caraway oil are used for this experiment. These samples can be found in a small box near GC\#3.

Isolation by Gas Chromatography:

Inject 10 \(\mu\)L of spearmint oil into the gas chromatography column. Limonene comes out first followed by (\(-\)) carvone. Just as either component of the oil starts to elute as evidenced by the start of a chromatographic peak, install a 3 mm o.d. by 10 cm gas collection tube at the sample exit port (HOT!) by pushing it only 1/4\” into the rubber septum with a hole in it. Remove the tube for that component as soon as the recorder reaches baseline again. You will need 2 collection tubes, one for limonene and one for (\(-\))-carvone. For NMR and IR analysis, repeat the injection and collection 2 or 3 times, collecting the eluted peaks in the same marked tubes, so that sufficient material is available for either analysis. One shot is usually sufficient to obtain enough material for GC-MS.

This procedure is repeated to isolate (\(+\))-carvone by injection of caraway-seed oil.

Cleaning Up:

Dispose of NMR or GC-MS samples in the Halogenated Organics Container.

Analysis:

Perform odor tests of both carvone isomers by sticking a thin strip of filter paper into the collection tube and absorbing a tiny amount of the liquid onto it. Withdraw it and waft the filter paper by your nose. Have others try it. About 8 to 10\% of the population cannot detect the difference in the odors of optical isomers. Most people, however, find the difference to be quite obvious.

Run analyses of both the (\(+\))- and (\(-\))-carvone enantiomers and limonene. To run an NMR, wash the liquid out of the collection tube directly into an NMR tube with deuterated chloroform. To run IR spectra, put a drop of each compound onto a salt plate. For GC-MS analysis, wash each tube’s contents into a shorty vial with \(\text{CH}_2\text{Cl}_2\) until the vial is almost full.

Final Report:

Label relevant peaks on all spectra, include labelled chromatograms, and discuss the odor tests. Tell whether your analysis method could and did differentiate between the (\(+\)) and (\(-\)) enantiomers.

Postlab Questions:

1. Why would TLC not be so useful for this separation if you were going to run an NMR or IR?
2. Tell whether the carvone isomer shown below is R or S.