

Evaluating Peppermint Oils by Chiral GC/MS

Using an Rt-γDEXsa™ Column

By Julie Kowalski, Innovations Chemist


- Rt-γDEXsa™ column has unmatched selectivity for peppermint oil stereoisomers.
- GC/MS enables detailed comparisons of natural products.
- Analysis requires no sample preparation.

Peppermint has a long history as a flavor additive and herbal remedy. Ancient Greeks and Romans adorned themselves with peppermint leaves and used the oil to flavor sauces and wines.[1] Today, peppermint is widely used in foods, candies, alcoholic and non-alcoholic beverages, cosmetics, personal care products, perfumes and, of course, chewing gum. Modern research has demonstrated health benefits of peppermint include antispasmodic, carminative, cholagogue, antibacterial, secretolytic, and cooling activity.[2]

Peppermint oil is isolated from the plant *Mentha piperita*. Preparation begins with harvesting leaves and flowering tops from the plant. Although other techniques exist, steam distillation is the most commonly used method for extracting highly concentrated oil from the plant material.

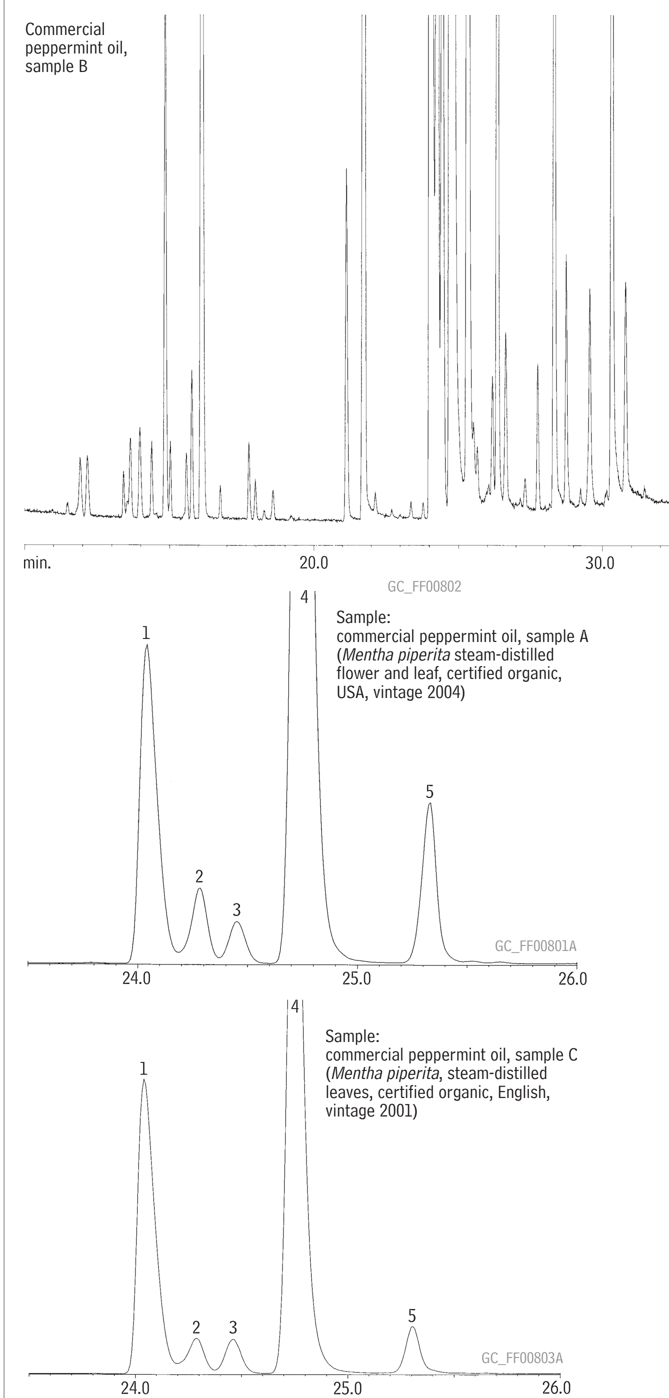
The use of peppermint oil in commercial goods and the rising demand for all-natural products drive a need for more rigorous testing. Often, a product is adulterated to increase desirable properties of the natural oil or to avoid costly manufacturing of all-natural oil. Adulteration usually is accomplished by adding a similar but cheaper oil, such as cornmint oil (*Mentha arvensis*), or by diluting the oil with various solvent oils. Adulteration and quality consistency of peppermint oil fuels concern over compromised quality, but also introduces health safety issues; for example, there is potential for an allergic reaction to an added unnatural compound or excess of a natural component.

Reliable, sensitive analytical methods are vital to detect complex manipulation of synthetic materials to mimic natural materials. Also, standardizing the composition that defines a "natural" product can be difficult, due to natural variation among plants and plant varieties, variation in geographical and seasonal factors, and inconsistencies in the manufacturing process. Some naturally occurring stereoisomers show greater biological activity than their counterparts: (-)-menthol, for example, is the stereoisomer known to have the greatest cooling and scent effects. This inequality between stereoisomers can be used to advantage, because reliable methods of analyzing specific chiral components can be used to monitor product quality.

Despite the value of identifying and quantifying major components like menthol, methone, and methyl acetate, dependable identification and quantification is difficult because each of these is represented by several stereoisomers. Menthol, for example, has three chiral centers, for a total of eight stereoisomers, making chromatographic separation difficult.

Here, we show a robust chiral GC/MS method that can be used with confidence to characterize and quantify stereoisomeric compounds. We purchased four peppermint oil samples from four commercial sources. Each sample was identified by information provided at time of purchase, including harvest location and year. Analyses were performed in triplicate on a Shimadzu GC/MS; model GC-17A, MS-QP5000, using an Rt-γDEXsa™ cyclodextrin-based column. The autosampler program included extensive rinsing with methylene chloride to prevent sample memory and syringe plugging. Data were analyzed using Shimadzu LabSolution, Version 1.20. Identifications of

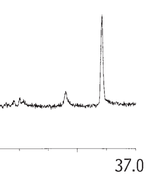
Figure 1 A representative commercial peppermint oil (sam
oils that differ in harvest location and year, using an Rt-γDE

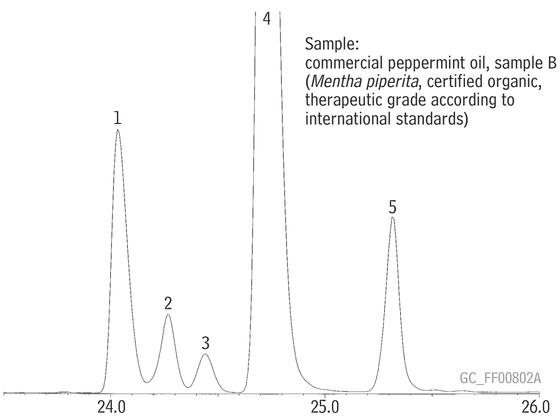


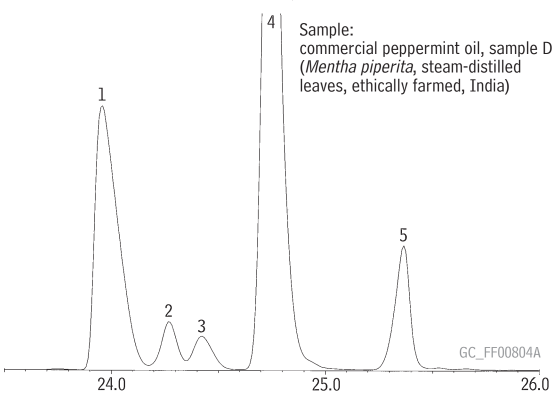
ple B), and major chiral components of four commercial
Xsa™ column.

Column:	Rt-γDEXsa™ 30m x 0.25mm ID, 0.25µm (cat.# 13113)
Inj.:	1.0µL neat, split (split ratio 1:150)
Inj. temp.:	230°C
Carrier gas:	helium, constant pressure
Flow rate:	35cm/sec. at 100°C
Oven temp.:	40°C to 120°C @ 5°C/min. to 135°C @ 3°C/min. to 200°C @ 5°C/min.
Det:	MS
Transfer line temp.:	200°C
Scan range:	40-300amu
Ionization:	EI
Mode:	scan

1. menthone
2. menthol
3. menthone
4. menthol
5. menthyl acetate







menthol, methone, and methyl acetate isomers were based on retention time comparisons to literature values and a mass spectra library search.[3] Integration of chromatograms was consistent. Additional menthol isomers were detected, but chromatographic conditions were optimized for those in Figure 1.

The figures show the Rt-γDEXsa™ phase is well suited to separating the stereoisomers of the major chiral components, and enables the analyst to differentiate among peppermint oils from different sources, and between peppermint oil and cornmint oil.* These chromatograms are similar, despite differences in harvest location, as illustrated by commercial samples A, C, and D. Similarity extends to samples which were harvested in different years, as shown by commercial samples A and C.

The Rt-γDEXsa™ phase allows detection of major components important to the quality of peppermint oil product, thus providing manufacturers and buyers with consistent profiles with which to confirm and track product quality. We offer a broad range of cyclodextrin-based chiral columns for analyzing oils or other enantiomer-containing materials. These columns are available individually or in kits that can help you select the best column, or combination of columns, for a particular application. In addition, our experienced Technical Service and Innovations chemists are always ready to help you resolve concerns about your particular chiral analysis.

References

1. http://www.botanical.com/botanical/mgmh/m/mints-39.html#pep)
2. http://www.umm.edu/altmed/ConsHerbs/Peppermintch.html
3. J. Chromatogr. A, 1054: 87-93 (2004).

Rt-γDEXsa™ Columns (fused silica)

(2,3-di-acetoxy-6-O-*tert*-butyl dimethylsilyl gamma cyclodextrin doped into 14% cyanopropylphenyl/86% dimethyl polysiloxane)

ID	df (µm)	temp. limits	length	cat. #
0.25mm	0.25	40 to 230°C	30-Meter	13113
0.32mm	0.25	40 to 230°C	30-Meter	13112

Essential Oils Chiral Column Kits (fused silica)

Dimensions & Columns	cat.#
30m, 0.25mm ID, 0.25µm Rt-ßDEXsm™, Rt-ßDEXse™, Rt-ßDEXsa™, & Rt-ßDEXsp™ columns	13196
30m, 0.32mm ID, 0.25µm Rt-ßDEXsm™, Rt-ßDEXse™, Rt-ßDEXsa™, & Rt-ßDEXsp™ columns	13197

For many other chiral columns and kits, refer to our catalog, or visit our website.

for **more** info

*For a chiral analysis of cornmint oil, visit our website (search: GC_FF00805).