



Analysis of Essential Oil Enantiomers by Chiral GCxGC-TOFMS

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The quality of flavoring components is dependent on enantiomeric composition. Variations in enantiomeric ratios of specific components may be related to sensory characteristics, indicate substitution or adulteration, or may show improper storage and handling of the material. Enantiomers may be separated by GC if a chiral column is used. Even with enantiomers separated from each other, the coelution with other compounds can prevent accurate measurement of enantiomer ratios. With the structural similarities of compounds contained in mixtures such as peppermint oil or natural menthol, separation of enantiomers may be obtained, but other undesired coelutions still occur. The application of GCxGC increases the peak capacity of the chromatographic system. A chiral column is used in the first chromatographic dimension and an achiral column is used for the second chromatographic dimension. With coelutions resolved, enantiomer ratios may be calculated free from interference.

Experimental Conditions

GCxGC: Primary column: Restek Rt-BetaDEXsm 30 m × 0.25 mm ID × 0.25 μm

1st oven: 80 °C (1min hold) to 220° at 5 °C/min, then hold for 5 min.

Secondary column: Restek Rtx-17 0.75 m × 0.25 mm ID × 0.5 μm

2nd oven: 40 °C warmer than primary oven throughout.

Injection: 0.2 ml with a split ratio of 1:200 Inlet temperature: 220°C

Carrier gas: 1.4 ml/min constant He flow

Modulation period: 3.5s

TOFMS: Electron Ionization at 70eV

Mass range (u): 35 to 350

Acquisition rate: 200 spectra/s

Results

One-dimensional chromatography of peppermint oil on the Rt-BetaDEXsm column results in coelution between menthyl acetate and (+)-menthol. With the similarities in spectra between menthol and menthyl acetate, there is no way to determine the relative amounts of the menthol isomers and menthol acetate present in the sample by GC separation using this column. GCxGC separation of peppermint oil is shown in Figure 1. With the addition of the second chromatographic dimension, menthol acetate is clearly separated from menthol along the second chromatographic dimension.

GCxGC-TOFMS chromatography of solutions of (+)- and (-)-menthol showed the relative responses of the isomers accurately reflects the proportions of the isomers in the mixture. The percentage of each isomer accurately reflects the proportion of each isomer in the mixture.

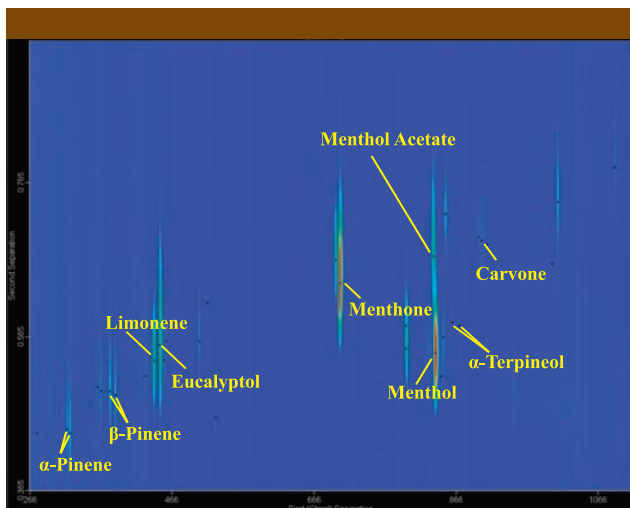


Figure 1: GCxGC Separation of peppermint showing enantiomeric pairs. In some cases the second enantiomer is not observed. Menthol acetate elutes in the first chromatographic dimension at the same location as (+)-menthol.

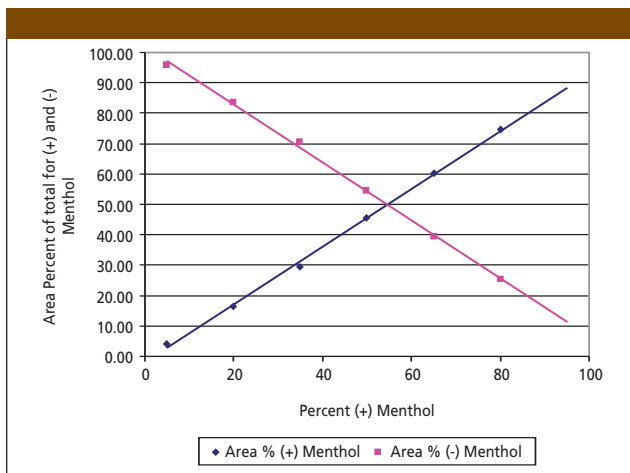


Figure 2: Linearity of response in measurement of enantiomer ratios.

Conclusions

The application of GCxGC to chiral separations provides the ability to obtain accurate enantiomer ratios even when interferences would otherwise coelute on the chiral column.

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