Comparison of the Analysis of California Lemon Oil: GC-FID vs. GCxGC-FID

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Key Words: FID, Quantification, GC, GCxGC

1. Introduction

Essential oils are complex mixtures that can contain hundreds of different compounds. Traditional analyses have been done with one-dimensional gas chromatography. The increase in detectability, resolution, and peak capacity offered by GCxGC allows for the potential to characterize a complex sample in a single analysis.

2. Instruments and Methods

In this study, measurements were made with a LECO GCxGC-FID system. This system consists of an Agilent 6890 gas chromatograph equipped with a LECO quad jet dual-stage modulator. Detection is by an Agilent 6890 Flame Ionization Detector operated at 200 Hz. For all analyses in this study, the primary column was a 10.0 m x 0.18 mm ID x 0.18 µm df Rtx-5, and the secondary column was a 1.0 m x 0.10 mm ID x 0.1 µm df Rtx-1701. The transfer line from the end of the secondary column to the FID was a 20 cm section of 0.25 mm ID uncoated fused-silica capillary. For one-dimensional analyses, the modulator's jets were turned off with the system treated as a dual-column ensemble.

For non-quantitative analyses, neat 1 µL samples were injected using the split mode of the split/splitless inlet with a split ratio of 300:1. For quantitative analyses, lemon oil was diluted in dichloromethane and 1 µL was injected in splitless mode. For both GC and GCxGC analyses, lemon oil was analyzed by both methods under conditions optimized for GC and optimized for the GCxGC with a 6 second modulation period.

3. Results

The total number of peaks with S/N ratios of >200, >100, and >50 were determined for each technique. The results are included in Table 1.

Table 1: Summary of peak counts at varying S/N ratios

	# peaks S/N >200	# peaks S/N >100	# peaks S/N >50
GCxGC-FID	241	243	244
GC-FID	103	146	187

For the GC analyses, a four-fold increase in the desired S/N ratio leads to a nearly 50% decrease in the number of peaks observed. For the same increase in desired S/N ratio, the GCxGC analyses showed a decrease of <0.5%. For the more stringent S/N requirement of >200, the GCxGC method still detected nearly 30% more peaks than the GC method did at the least stringent S/N ratio of >50. A representative GC-optimized chromatogram is shown in Figure 1.

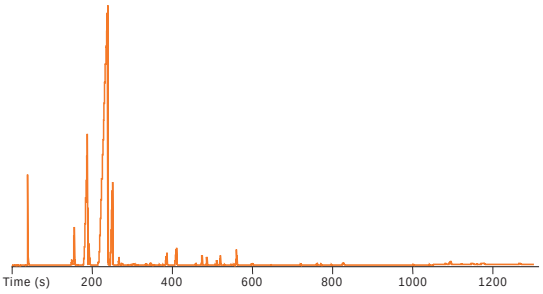


Figure 1: An optimized GC chromatogram for the TIC of 1 µL of lemon oil at a split ratio of 300:1.

A GCxGC-optimized contour plot of an identical injection is shown in Figure 2 with the inset area being a magnification of the indicated area on the Z-axis. A 3D plot of the same analysis is shown in Figure 3. A zoomed-in view of a sample area from Figure 3 is shown in Figure 4.

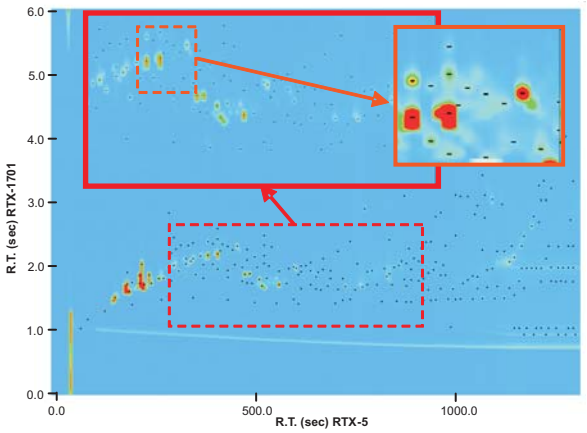


Figure 2: An optimized GCxGC contour plot of 1 µL of lemon oil at a split ratio of 300:1. The inset is a magnification of an area which highlights the enhanced separation in the second dimension.

Delivering the Right Results

Calibration curves were generated for β-pinene, limonene, and γ-terpinene. These three compounds were identified as the three major components of Lemon Oil by Chamblee et. al. (1991). All calibration curves ranged from 8.5 pg/μL to 85 ng/μL and had R2 values of >0.99923. Calibration curves for limonene and β-pinene are shown in Figure 5 and Figure 6. The results of the quantification are shown in Table 2. LOD's were extrapolated for a S/N ratio of 10. Another advantage of GCxGC is the structured nature of the chromatograms. Members of a homologous series (i.e. pentanone, hexanone, heptanone, octanone, etc.) will elute in such a fashion as to form a diagonal band in the chromatogram. The most frequently observed of these is the nearly horizontal band formed along the bottom of the chromatogram that is comprised of the normal alkanes.

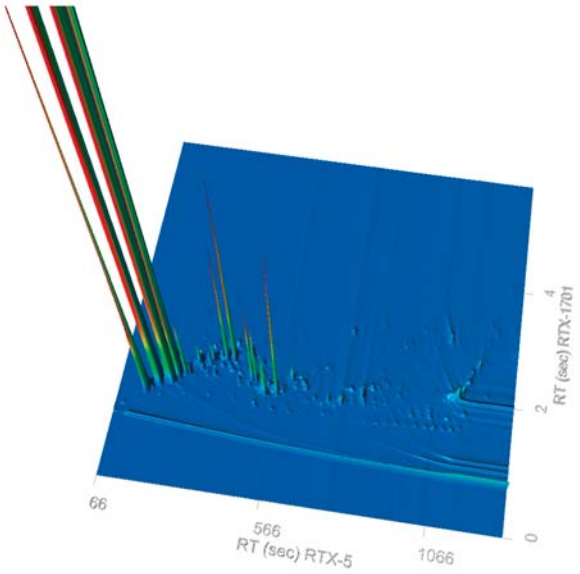


Figure 3: An optimized GCxGC 3D plot of 1 μL of lemon oil at a split ratio of 300:1. The Z-axis is scaled to show trace compounds.

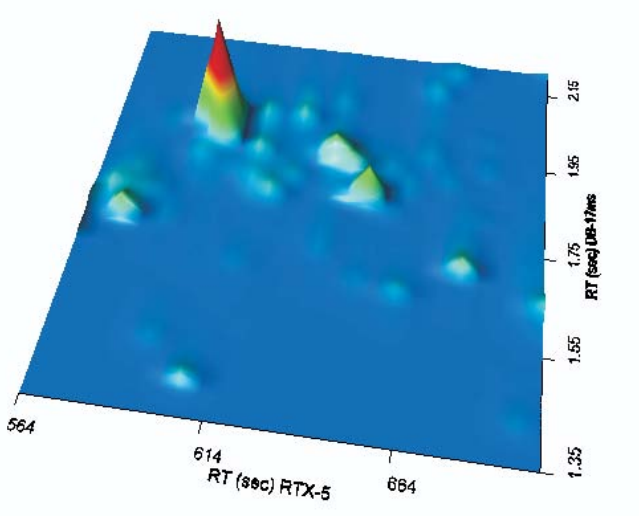


Figure 4: A zoomed-in view of the area in the box in Figure 3 showing greatly increased detectability offered by GCxGC.

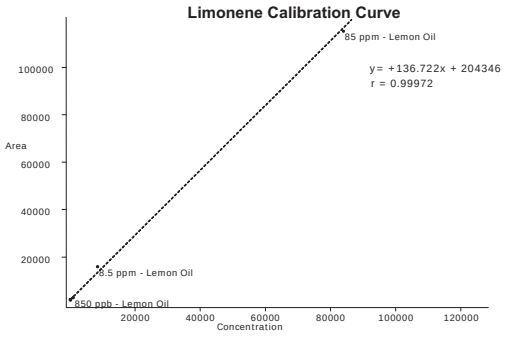


Figure 5: The calibration curve for limonene with concentrations from 8.5 ppb to 85 ppm.

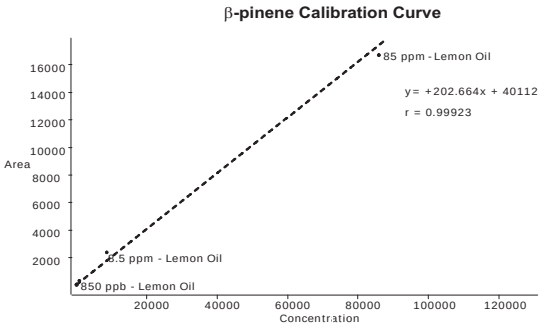


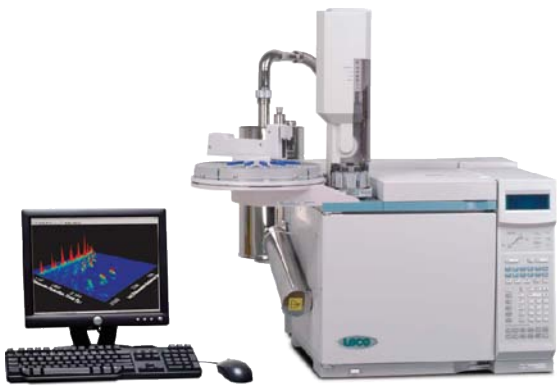
Figure 6: The calibration curve for b-pinene with concentrations from 8.5 ppb to 85 ppm.

Table 2: Lemon oil quantification results

Compound	Concentration (μg/μL)	LOD (pg/μL)
β-pinene	28.8	1.11
limonene	69.8	1.60
γ-terpinene	5.4	1.08

4. Conclusions

GCxGC has been demonstrated to provide advantages over traditional GC in the areas of improved detectability, increased resolution, and greater peak capacity. Through the utilization of these attributes, GCxGC can be used to characterize and quantify complex samples, such as essential oils, in a more expedient manner than is generally possible with a traditional one-dimensional analysis.



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Form No. 203-821-314 4/07-REV0