Characterization of a Biofuel Sample by Comprehensive Two-Dimensional Gas Chromatography Time-of-Flight Mass Spectrometry (GCxGC-TOFMS)

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Key Words: GCxGC, Time-of-Flight MS, Biofuels

1. Introduction

Biofuels are an increasingly popular source of energy worldwide. They are produced from several sources including vegetable oils, animal fats, and recycled greases. In order to be considered a biofuel, the fuel must contain 80 percent or more renewable materials. Production of biodiesel from recycled cooking oil is an example of an effort to utilize a product that has reached the end of its intended use cycle to provide renewable energy. Analytical methods utilized to characterize these products must be capable of identifying the hundreds to thousands of compounds often present in these extremely complex mixtures. The added resolving power and increased peak capacity of comprehensive two-dimensional gas chromatography (GCxGC) provides an effective separation of the components present in these products. This application note will show an example of the chromatographic separation attainable with GCxGC as well as identification of compounds using a time-of-flight mass spectrometer (TOFMS).

2. Sample

A Biofuel sample was diluted in methylene chloride prior to analysis on a LECO Pegasus® 4D GCxGC-TOFMS instrument.

3. Experimental

A LECO Pegasus 4D GCxGC-TOFMS system was used for this analysis using the system conditions detailed below.

GC:
  Agilent 6890 w/LECO dual-stage, quad-jet thermal modulator and secondary oven
Column 1:
  Rtx-50 DHA, 50 m x 0.20 mm x 0.5 μm
Primary Oven:
  35°C hold 2 min, 5°C/min to 300°C, hold 15 min
*Column 2:
  BPX-50, 1.25 m x 0.1 mm x 0.1 μm
Secondary Oven:
  +5°C offset from main oven
Injection:
  0.05 μL, split 250:1 at 200°C
Carrier Gas:
  Helium at 1.0 ml/min
Modulator Temperature Offset: 25°C
Modulation Period:
  3s with a 0.6 s hot pulse time

MS:	LECO Pegasus 4D
Acquisition Delay:	0 seconds
Saved mass Range:	29 to 500 m/z
Acquisition Rate:	200 spectra/second
Source Temperature:	225°C

**The columns used for this analysis were connected using the NLISIS Meltfit One (see Fig. 1). The system remained leak free for the duration of the project.*

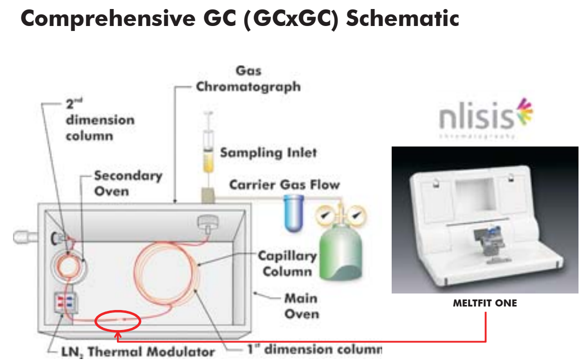

Figure 1. Comprehensive GCxGC schematic showing location of MeltFit Connector.

4. Results

The results for the analysis of this biofuel sample are shown in figures 2 and 3. The figures represent GCxGC contour plots which show components detected in the sample which were separated on two chromatographic planes. The x-axis in the contour plots represents a chromatographic separation on a non-polar (Rtx-50 DHA) column and the y-axis represents a chromatographic separation on a polar (BPX-50) column. Notice the total ion contour plot in Figure 2 that compounds are displayed in a structured nature. Higher boiling point compounds elute later in the 1st dimension (x-axis), while the more polar analytes elute later (towards the top) in the 2nd dimension (y-axis). Figure 3 shows the extracted ion chromatogram (XIC) for m/z 57 and 74 displaying a portion of the alkanes and fatty acid methyl esters (FAMEs) detected in this mixture. Notice how these compounds are effectively separated in the second dimension. These compound classes often co-elute in one-dimensional GC separations.

Delivering the Right Results

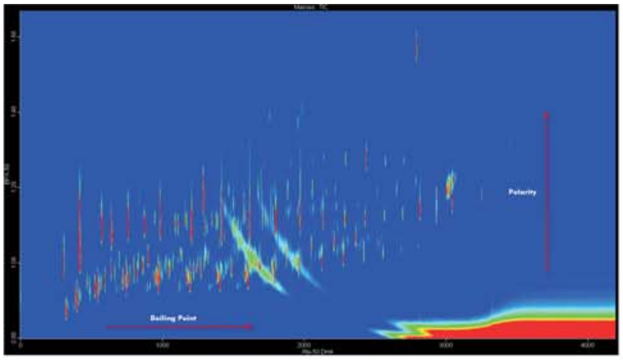

Figure 2. Total ion contour plot showing highly structured nature of a GCxGC contour plot.

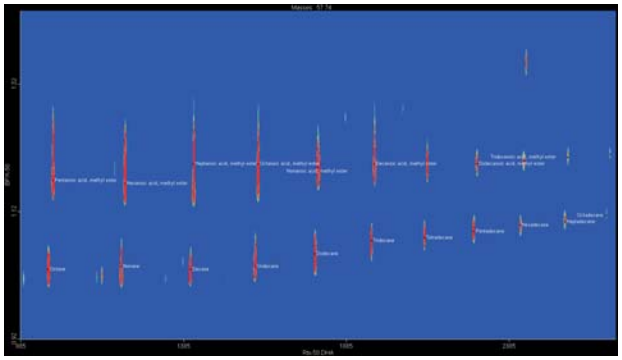

Figure 3. XIC showing contour plot for m/z 57 and 74 which highlights a portion of the alkanes and FAMES which were identified in this mixture.

5. Conclusions

This application shows the utility of GCxGC-TOFMS for characterization of biofuel type samples. The enhanced peak capacity of the GCxGC separation is critical to eliminating many of the co-elution issues associated with the analysis of these sample types with one-dimensional GC systems.

In addition to the increase in chromatographic resolution, the use of a TOFMS provides the ability to acquire full mass range spectra without sacrificing speed or sensitivity. This is beneficial for accurate identification of compounds in these complex sample types.

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Form No. 203-821-396 10/10-REV0