

Petroleum Analysis Using the LECO[®] Pegasus[®] 4D GCxGC-TOFMS System

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1. Introduction

A series of Petroleum samples of varying volatility and carbon number were evaluated using the Pegasus 4D GCxGC-TOFMS system. Gasoline was analyzed as an example of a fairly volatile petroleum product. Diesel was analyzed as an example of a petroleum product with intermediate volatility. Finally, a paraffin sample was analyzed as an example of fairly low volatility petroleum product. The chromatographic resolution advantages of the GCxGC-TOFMS technique were investigated along with basic system performance across the wide volatility range represented in these three products.

2. Experimental Conditions

Gasoline

GC:

Agilent 6890 Gas Chromatograph equipped with a LECO GCxGC Thermal Modulator

Injection:

Split Injection (200:1) at 250°C, 0.2 l

Primary Column:

Agilent 50 m x 0.2 mm (0.5 m) PONA

Secondary Column:

Agilent 2 m x 0.1 mm (0.1 m) DB-WAX

Carrier Gas:

Helium, 1.5 ml/minute constant flow

Primary Oven Program:

50°C (0.2 minute) to 200°C at 1.5°C/minute

Secondary Oven Program:

55°C (0.2 minute) to 200°C at 1.5°C/minute

Modulator Offset: 30°C

Modulation Frequency: 5 seconds

Hot Time: 0.5 seconds

MS: LECO Pegasus 4D GCxGC-TOFMS

Ionization: Electron Ionization at 70eV

Source Temperature: 225°C

Stored Mass Range: 35 to 500 u

Acquisition Rate: 100 spectra/second

Diesel

GC:

Agilent 6890 Gas Chromatograph equipped with a LECO GCxGC Thermal Modulator

Injection:

Split Injection (100:1) at 250°C, 0.2 l

Primary Column:

Agilent 50 m x 0.2 mm (0.5 m) PONA

Secondary Column:

Agilent 2 m x 0.1 mm (0.1 m) DB-WAX

Carrier Gas:

Helium, 1.5 ml/minute constant flow

Primary Oven Program:

100°C (0.2 minute) to 240°C (56 min) at 1.5°C/minute

Secondary Oven Program:

110°C (0.2 minute) to 240°C (56 minute) at 1.5°C/minute

Modulator Offset: 30°C

Modulation Frequency: 5 seconds

Hot Time: 0.6 seconds

MS: LECO Pegasus 4D GCxGC-TOFMS

Ionization: Electron Ionization at 70eV

Source Temperature: 225°C

Stored Mass Range: 35 to 500 u

Acquisition Rate: 100 spectra/second

Paraffin

GC:

Agilent 6890 Gas Chromatograph equipped with a LECO GCxGC Thermal Modulator

Injection:

Split Injection (300:1) at 300°C, 0.2 l

Primary Column:

Agilent 30 m x 0.32 mm (0.25 m) DB-5

Secondary Column:

Restek 2 m x 0.1 mm (0.1 m) Rtx-50

Carrier Gas:

Helium, 1.9 ml/minute constant flow

Primary Oven Program:

40°C (2 minutes) to 325°C (10 minutes) at 2°C/minute

Secondary Oven Program:

70°C (2 minutes) to 325°C (10 minutes) at 2°C/minute

Modulator Offset: 60°C

Modulation Frequency: 6 seconds

Hot Time: 2.4 seconds

MS: LECO Pegasus 4D GCxGC-TOFMS

Ionization: Electron Ionization at 70eV

Source Temperature: 200°C

Stored Mass Range: 50 to 600 u

Acquisition Rate: 100 spectra/second

3. Results

Qualitative analyses of all three petroleum samples were conducted. Figure 1 indicates the reconstructed total ion current chromatogram (TIC) obtained from the gasoline sample. The aromatic regions are easily separated from each other and the aliphatic portion of the chromatogram. Total aromatic content and BTEX content can be easily determined from the analysis. Structural classes are grouped in bands for easy identification of individual analytes or structural classes. The GCxGC Thermal Modulation system was able to easily trap the higher volatility aliphatics and aromatics commonly found in gasoline. The conditions were optimized for aromatic separation in this particular analysis. A choice of a different secondary column type and conditions would provide greater separation of the aliphatic classes in the chromatogram. Other analyses with the Pegasus 4D system have shown that a DB-17 phase, used in place of the DB-WAX phase shown in this analysis, will provide enhanced aliphatic resolution.

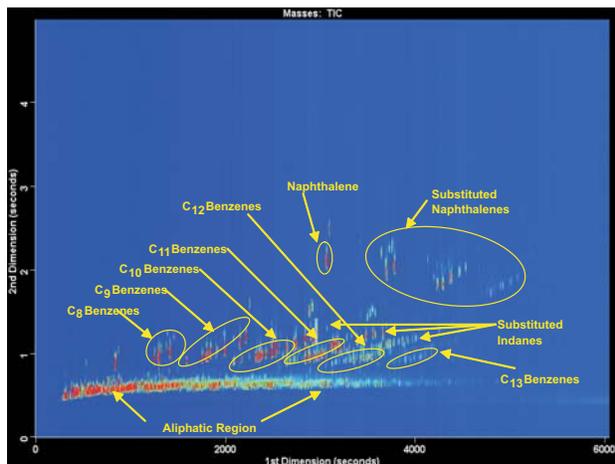


Figure 1. Gasoline GCxGC-TOFMS Total Ion Chromatogram.

Analysis of the diesel sample showed similar results to those obtained from the gasoline analysis. The GCxGC Thermal Modulation system was easily able to handle the intermediate volatility range of the sample. Excellent peak shapes were obtained across the volatility and concentration range of the sample. The emphasis in this separation was once again the separation of the various classes of aromatic compounds from each other and the aliphatic region of the chromatogram. Figure 2 shows the TIC from the GCxGC-TOFMS separation of the diesel sample. The aromatic structural classes are well grouped in chromatographic bands for easy identification. This particular diesel sample was obtained prior to the desulfonation step in the production process. A number of sulfur classes have been identified within the chromatogram.

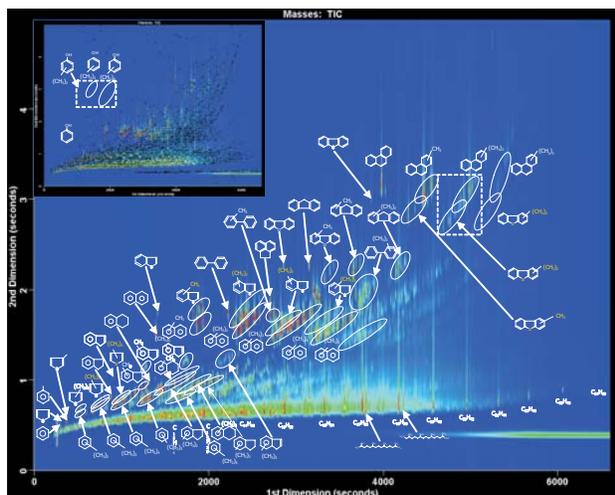


Figure 2. Diesel GCxGC-TOFMS Total Ion Current Chromatogram. Sulfur containing analyte classes are highlighted with yellow structures.

The analysis of the paraffin sample proved to be more challenging. The larger and less volatile molecules found in the paraffin required some modification of the GCxGC Thermal Modulator conditions. Hotter modulator temperatures were used to increase the temperature of the hot jet for more efficient release of the higher boiling analytes. The time the hot jet was applied in the modulator sequence, designated as the Hot Time in the method, was also increased to facilitate release of the higher boilers.

The higher temperature requirements for the secondary separation preclude the use of a WAX phase. Instead an Rtx-50 phase, stable to 320°C, was used.

Figure 3 shows the TIC for the paraffin sample, and Figure 4 shows the TIC for the paraffin sample along with the peak markers indicating the positions of all analytes automatically located using the LECO ChromaTOF Peak Find algorithm.

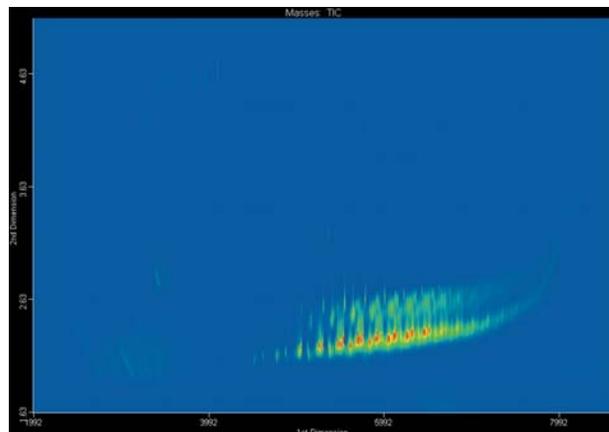


Figure 3. Paraffin Total Ion Current Chromatogram.

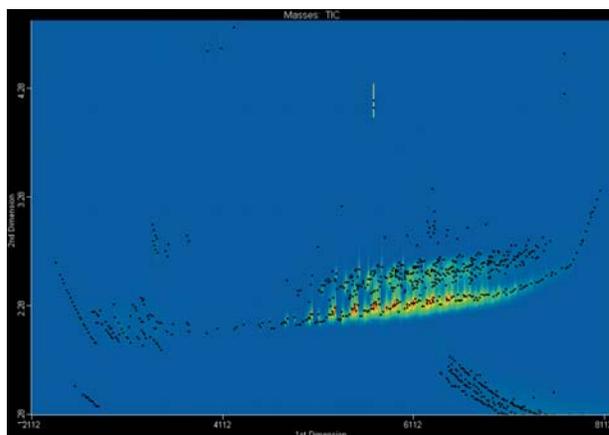


Figure 4. Paraffin Total Ion Current Chromatogram with Peak Markers (black dots).

The Automated Peak Find algorithm automatically locates all peaks detected in the chromatogram that meet the operator's specifications for signal-to-noise threshold and expected peak width. The peak width defines the duration of an event before it can be considered a possible peak. The signal to noise threshold specifies how large a peak must be to be included in the report. Once peaks are located, the mass spectrum for the analyte is calculated. Background signal is subtracted and interfering signals from coeluting analytes are automatically deconvoluted away to yield a clean spectrum for more accurate analyte identification. In the case of GCxGC data an additional step is performed. The ChromaTOF software automatically searches the GCxGC data to determine where peaks in the first dimension have been modulated multiple times. Based on retention time in the second dimension and mass spectral match, the software automatically combines the modulated peaks into a single peak reported in the peak table. The elimination of modulated peaks greatly simplifies the review of GCxGC data.

The pattern of the peak markers shows several distinct regions in the chromatogram. The concentrated region of the chromatogram (red) corresponds to the normal and iso-paraffin region of the paraffin sample. Figure 5 shows an enhanced view of this region of the chromatogram.

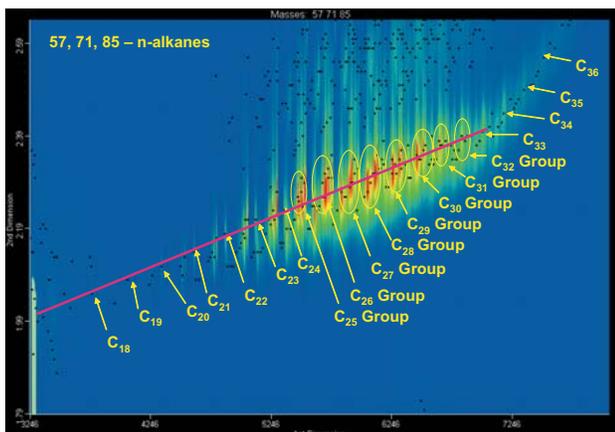


Figure 5. Enhanced view of the aliphatic region of the Paraffin sample.

The first dimension chromatographic conditions provide a good separation of analytes based on carbon number. The Rtx-50 phase provided improved resolution in the second dimension for the paraffin and iso-paraffin region of the chromatogram. Iso-paraffins are resolved away from the normal paraffins.

Alignment of the normal paraffin region is lost at the higher carbon numbers in Figure 5. At this point in the chromatogram the oven has reached its maximum ramp rate and has begun an isothermal hold at 320°C. Since the temperature of the separation is no longer increasing with the polarity of the analytes, the linear relationship is disrupted, leading to the upward curve at higher carbon numbers. If higher carbon numbers need to be analyzed, a possible solution would be the use of higher temperature phases in the first and second dimensions. However, higher temperature phases, especially a phase with a polarity comparable to the Rtx-50, are not readily available. If a sacrifice in carbon number resolution could be tolerated, reducing the length of the first dimension column would also provide some benefit. The higher carbon number analytes would elute from the first dimension column earlier, and perhaps during the temperature ramp step of the oven program.

Figures 6 and 7 indicate the positions of the di-naphthene analytes in the chromatogram. The di-naphthenes and other cyclic structures are well resolved from the normal paraffin and iso-paraffin regions of the sample.

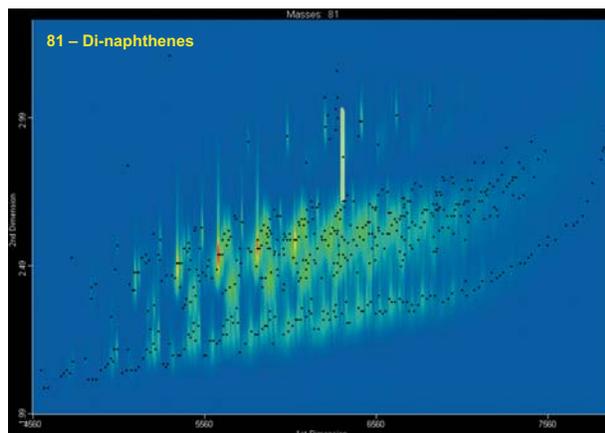


Figure 6. Selected ion profile chromatogram for mass 81 indicating a band of di-naphthene analytes in the Paraffin sample.

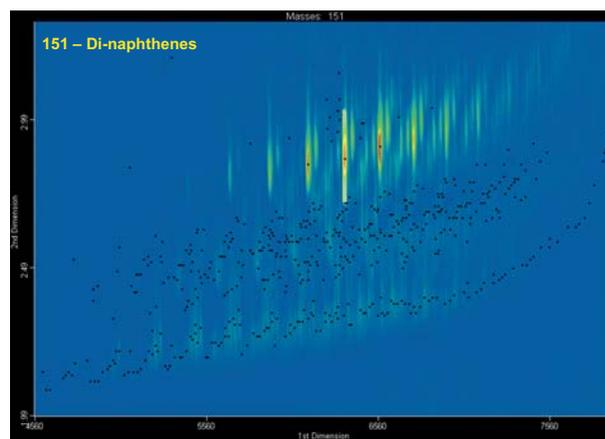


Figure 7. Selected ion profile chromatogram for mass 151 indicating a band of di-naphthene analytes in the Paraffin sample.

Other more polar analytes are resolved at the upper end of the chromatogram. Some possible identifications for these analytes are shown in Figure 8.

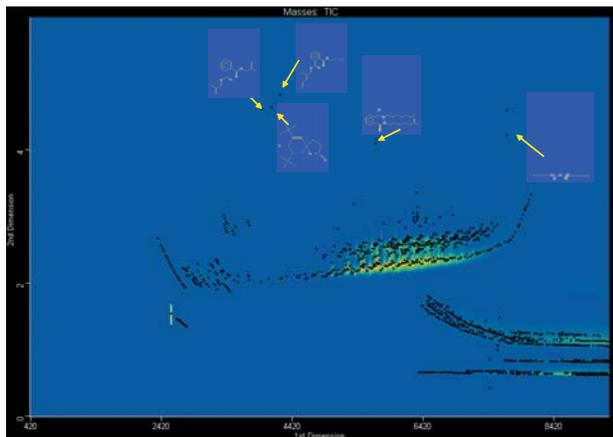


Figure 8. Possible identifications of other polar analytes located in the Paraffin sample.

4. Conclusions

The LECO Pegasus 4D GCxGC-TOFMS system provides a significant increase in chromatographic resolution for petroleum analyses across a wide volatility range. The feasibility of total aromatic, BTEX, and oxygenate measurements in a single injection has been demonstrated for gasoline. More complete characterization of diesel fuel, including identification of several classes of sulfur compounds, is also easily achieved using the Pegasus 4D. Finally, more detailed higher temperature separations of normal paraffins, iso-paraffins, and naphthenic paraffins can also be obtained using the LECO Pegasus 4D system.

The benefit of the automated data processing algorithms in the ChromaTOF software was also demonstrated for the analysis of complex petroleum samples. Automated Peak Find algorithms locate all peaks in the chromatogram, including those that coelute with other analytes or are buried beneath the baseline of the TIC. The automated Mass Spectral Deconvolution algorithm automatically extracts clean analyte spectra free of background signal or interferences from coeluting analytes. Finally, the Combine algorithm for GCxGC separations automatically locates peaks that have been modulated multiple times and combines them into a single entry in the peak table for simplified data review.



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