Automated Characterization of a Diesel Sample Using Comprehensive Two-Dimensional GC (GCxGC) and Time-of-Flight Mass Spectrometry (TOFMS) Detection (Pegasus® 4D System)

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Key Words: GCxGC-TOFMS, Petroleum, Classifications

1. Introduction

The high complexity of diesel samples makes them good candidates for two-dimensional comprehensive gas chromatography (GCxGC). In addition to the challenge created by the presence of thousands of components, each of the analytes is of importance to the petroleum industry and cannot be treated as interference. The need for complete characterization of the analytes has led to an increase in the interest of coupling mass spectrometry to GCxGC systems.

Components that elute from the first column of a GCxGC system are thermally modulated and sharp eluent pulses enter the second column of the system. This results in very narrow chromatographic peaks that have to be characterized after elution from the secondary column, and consequently fast data acquisition systems are needed for detection. LECO's Pegasus TOFMS is the only mass spectrometer capable of acquisition rates of 500 full spectra/second, adequate for the detection of peaks as narrow as 20 msec.

The purpose of the analysis was a diesel sample obtained before removal of sulfur-containing components was analyzed for chemical class pattern identification.

2. Experimental Conditions

GCxGC:
  Agilent 6890 GC equipped with a LECO Thermal Modulator
Primary Column:
  DB-PONA, 50 m, 0.2 mm id, 0.5 μm film thickness
Main Oven:
  100°C (0.2 minute hold) to 240°C (66.7 minute hold) at 1.5°C/minute
Secondary Column:
  DB-WAX, 2 m, 0.1 mm id, 0.1 μm film thickness
Secondary Oven:
  110°C (1 minute hold) to 240°C (74.5 minute hold) at 1.5°C/minute
Inlet Temp: 250°C
Injection Size: 0.2μl
Split Ratio: 100:1
Carrier Gas:
  He at a constant flow of 1.5 ml/minute
Modulator Temp:
  30°C offset from main oven
Modulation Frequency:
  5 seconds with a 0.6 second hot pulse time

MS: LECO Pegasus® 4D GCxGC-TOFMS
Ionization: EI at 70eV
Mass Range (u):   35 to 500
Acquisition Rate: 100 spectra/second
Source Temp: 225°C

3. Results

One of the advantages of using GCxGC for chromatographic separation is the high degree of organization based on chemical structure that can be seen in the resulting chromatogram. Components from the same class are aligned in bands based on the two separation mechanisms used. This can be seen in Figure 1 where the total ion current (TIC) chromatogram of the diesel sample is displayed as a surface plot, and also in the contour plot displayed in Figure 2.
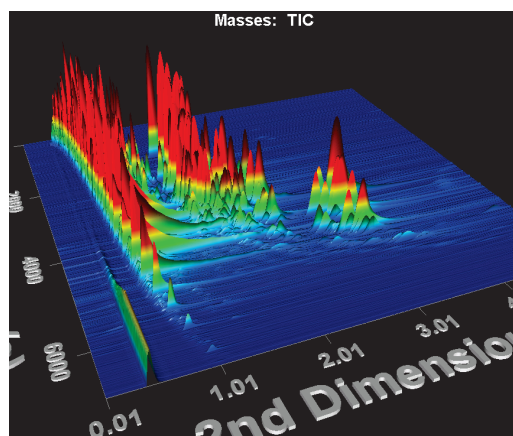

Figure 1. TIC chromatogram of a diesel sample prior to removal of the sulfur-containing components.

In Figure 2, chemical structures for groups of components present in different regions of the chromatogram are presented. As can be seen in this figure, the chromatogram is organized by carbon number in the first dimension (primary non-polar column), and by polarity in the second dimension (secondary polar column).
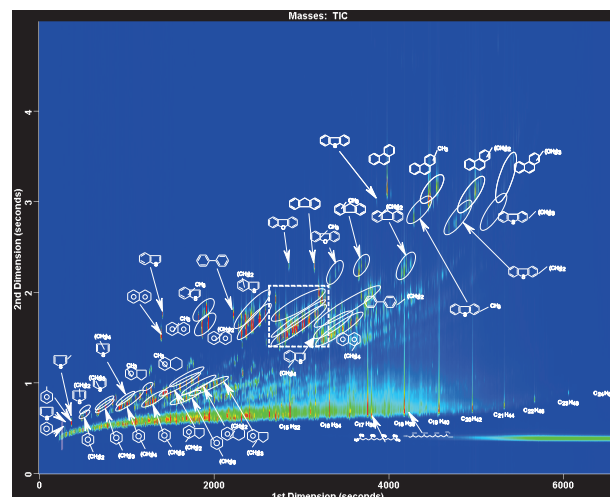

Figure 2. TIC chromatogram of the diesel sample presented as a contour plot. Chemical structures for different classes of components are also presented. Structures for sulfur-containing components are drawn in yellow for better visualization.

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As the structural complexity of the components increases, partial overlap for component classes can be seen even though GCxGC offers a tremendous increase in peak capacity. This can be easily resolved when a mass spectrometer is used for detection. An example is presented in Figure 3, which represents the region surrounded by a dashed line in Figure 2 on a smaller scale. Plotting unique m/z values for the different structural classes allows the analysts to identify three different classes when only one class seemed to be present in the TIC chromatogram.
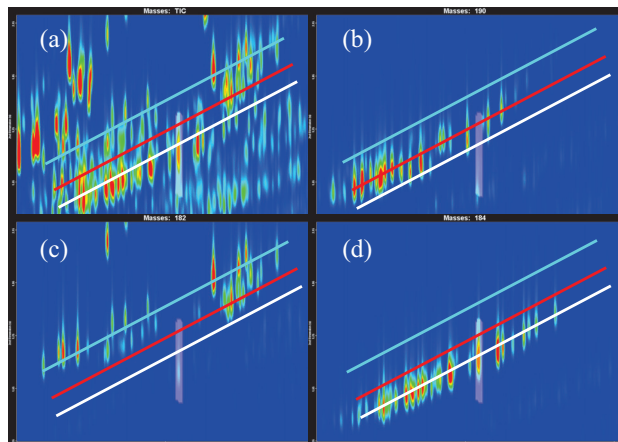

Figure 3. Reduced scale of the substituted benzothiophene (red line), substituted biphenyl (blue line), and substituted naphthalene (white line) region from Figure 2. TIC (a), as well as characteristic m/z values for C12 benzothiophene (b), C14 biphenyls (c), and C14 naphthalenes (d), are shown in the same region of the chromatogram.
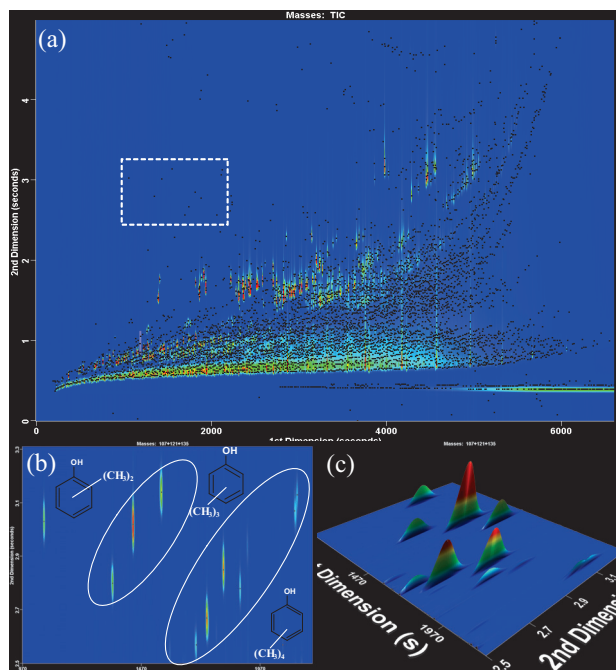

Figure 4. (a) TIC chromatogram for the diesel sample with peak markers for the found peaks represented as black dots. A selected region of the chromatogram for which a sum of m/z is shown is presented on a reduced scale as a contour plot (b) and as a surface plot (c). Chemical structures for the components of interest are also presented in part (b) of the figure.

More than 6,000 components were found to be present in the diesel sample when acquired data was processed at a S/N value of 500. Figure 4 shows an example of a region of the chromatogram where the found peaks do not appear to be actual peaks. This is caused by higher intensity peaks scaling the chromatogram and making the lower intensity peaks to be almost lost into the blue background. By plotting the sum of the unique ions for the peaks of interest, their appearance can be greatly enhanced. The black dots in parts (a) and (b) of the figure represent peak markers for the found peaks.

4. Conclusions

Comprehensive two-dimensional GC (GCxGC) provided the additional peak capacity necessary to resolve more than 6,000 components present in the diesel sample. The highly organized chromatogram based on chemical structure added more power to component identification by providing confirmation for the results obtained from the mass spectral data. On the other hand, the addition of TOFMS detection to GCxGC technique proved to be a powerful tool in solving class identification for regions of the chromatograms where two or more chemical classes of components overlapped. In conclusion, GCxGC and TOFMS are complementary, allowing complete and automated characterization of the complex diesel sample.