Classification of Compounds in a Diesel Sample Using GCxGC-FID Analysis and Automated ChromaTOF® Data Processing

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Key Words: GCxGC-FID, Petrochemical

1. Introduction

Petroleum-type samples are the perfect candidates for comprehensive two-dimensional GC (GCxGC) analysis. Not only is the sample complexity very high (hundreds and even thousands of analytes are present), resulting in numerous coelutions in a one-dimensional analysis, but also there are numerous isomers present. The big differences in concentration for the analytes present result in masking the less intense peaks by the high-concentration analytes.

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 Program:
100°C (0.2 minute hold) to 240°C (67 minute hold) at 1.5°C/minute

Secondary Column:
DB-WAX, 1.7 m, 0.1 mm id, 0.1 µm film thickness

Secondary Oven Program:
10°C offset from main oven

Inlet Temperature:	250°C
Injection Size:	0.2 µl
Split Ratio:	100:1
Carrier Gas:	He at a constant flow of 1.5ml/min

Modulator Temperature:
30°C offset from main oven

Modulation Frequency:
5 seconds with a 0.6 second hot pulse time

Detector Type:	FID
Detector Temperature:	250°C
Data Collection Rate:	200 Hz

3. Results

A diesel sample obtained before the removal of sulfur-containing components was analyzed using the conditions described above. The highly structured chromatogram obtained from the analysis allows grouping based on the chemical structure of the compounds present in various regions of the chromatogram.

A new feature of the ChromaTOF® software enables the user to create class as well as subclass regions inside an acquired chromatogram. The classes are created by actually drawing rounded shapes around the groups of peaks of interest. The classes created can then be used in three different ways in the Data Processing method.

- If the classes created are hashed out, these regions of the chromatograms will be omitted from data processing (no peaks will be located automatically by the software).
- If the classes created are not hashed out, the data can be processed for the entire chromatogram with the peaks located inside the selected regions classified inside the peak table.
- If the classes created are not hashed out, the processing of the data can be done selectively inside of these regions.

After a template with the drawn classes is created, it can be applied to other samples for comparison purposes.

As can be seen from the experimental section, the column set used for the analysis of the diesel sample generated a boiling point (carbon number) separation in the first dimension, and a polarity separation in the second dimension. Based on this two-dimensional structure of the chromatogram, two different types of classes were generated. The first set of classes was based on the number of carbon atoms present in the molecule, and the second set of classes was based on the presence of sulfur in the molecule.

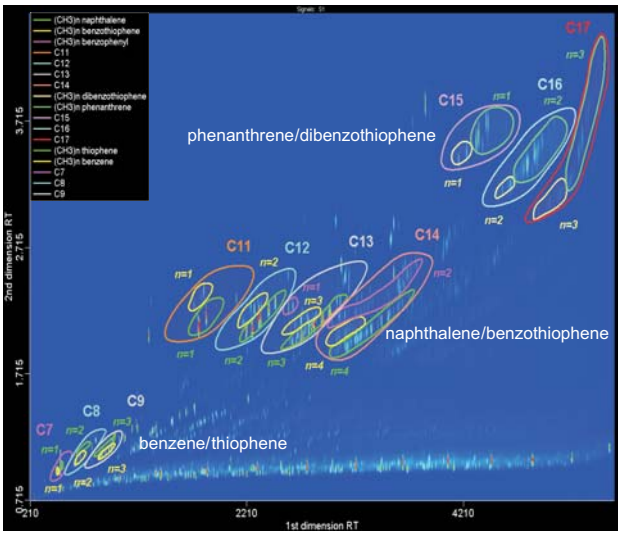

Figure 1. Contour plot chromatogram of a diesel sample obtained prior to the removal of the sulfur-containing compounds.

Figure 1 shows the two-dimensional chromatogram (contour plot) of the sulfur-containing diesel sample. Retention time in the first dimension is shown on the x-axis, retention time in the second dimension is shown on the y-axis, while signal intensity is illustrated on a color scale (blue represents the baseline, and red represents the most intense peaks in the chromatogram). For ease-of-viewing only some of the regions present were drawn into classes. Inside each Cn class a sulfur-containing (yellow line) and a carbon-only (green line) class is present. The n=x label shows the total number of carbons substituted on the ring.

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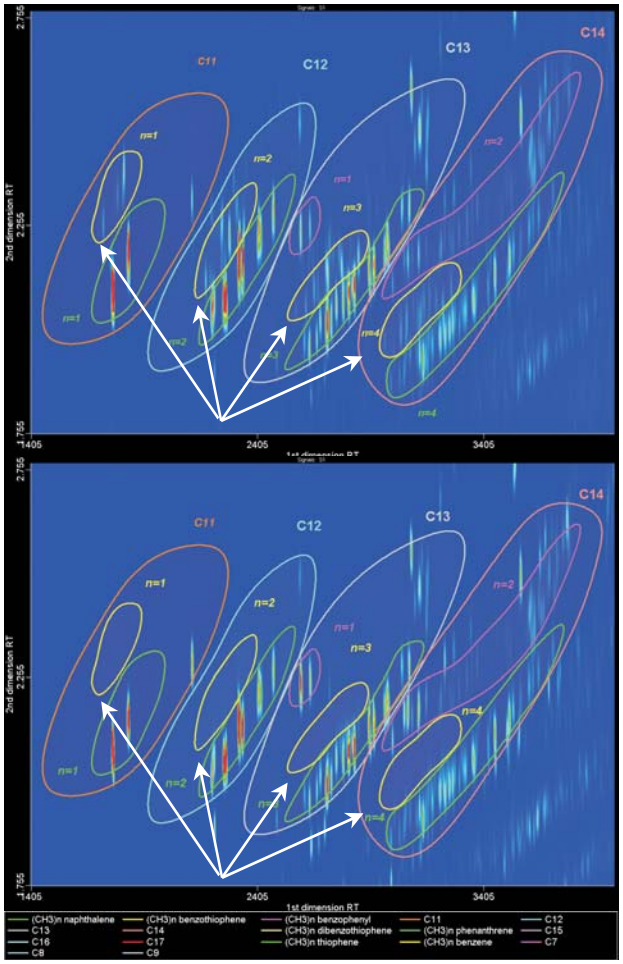

Figure 2. Substituted naphthalene/benzothiophene region with classes drawn for some of the sulfur-containing and carbon-only compounds for the sulfur-containing diesel sample (upper) and the sulfur-free diesel sample (lower).

Figure 2 shows an example of a part of the classification template created within the sulfur-containing diesel sample chromatogram, and then applied to a chromatogram obtained from the analysis of a sulfur-free diesel sample. Arrows point to the four regions where the sulfur compounds should be present.

Results obtained in the peak table after data processing can also be filtered to display only selected classes. The total for the selected class can also be calculated and displayed automatically. Figure 3 shows an example of the peak table display after a filter was applied to selectively display the C11 class.

Peak Table - "UOP Diesel:2"

Peak #	Name	Classifications	R.T. (s)	Area
32	Unknown 32	(CH3)n benzotiophene; C11	1725 , 2.255	38952
33	Unknown 33	(CH3)n naphthalene; C11	1760 , 2.070	74148
34	Unknown 34	(CH3)n naphthalene; C11	1765 , 2.120	1301866
35	Unknown 35	(CH3)n benzotiophene; C11	1785 , 2.325	30415
36	Unknown 36	(CH3)n benzotiophene; C11	1810 , 2.340	30906
37	Unknown 37	(CH3)n benzotiophene; C11	1815 , 2.390	86726
38	Unknown 38	(CH3)n naphthalene; C11	1830 , 2.175	107312
39	Unknown 39	(CH3)n naphthalene; C11	1835 , 2.210	622412
40	Unknown 40	(CH3)n naphthalene; C11	1950 , 2.210	1986.0
41	Unknown 41	C11	2115 , 2.320	80305
42	Unknown 42	C11	2115 , 2.480	3895.0
47	Unknown 47	C11	2210 , 2.505	1537.0
*	Total			2380460

Figure 3. Peak table filtered to show only C11 class compounds.

4. Conclusions

The highly structured chromatograms obtained from the analysis of petroleum samples using GCxGC enables the possibility of classifying the compounds into structure-based chemical classes. The ChromaTOF software allows the user to draw well-defined shapes (classes) around groups of peaks using acquired chromatograms. Once a classification template is created, it can then be applied to subsequent chromatograms for comparison purposes.

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