Diesel Fuel Classification Analysis Using GCxGC/FI and Kendrick Mass Defect Plots

Introduction

Comprehensive 2D gas chromatography (GCxGC) in combination with high-resolution mass spectrometry is a powerful tool for the analysis of complex mixtures.

In this work, we analyzed a diesel fuel sample by using GCxGC in combination with a new high-resolution time-of-flight mass spectrometer (HRTOFMS). Field ionization (FI) produced molecular ions for all components and exact mass measurements were used to obtain elemental compositions. A traditional Kendrick Mass Defect (KMD) plot was used to identify hydrocarbon groups in the diesel fuel sample.

Experimental

A commercially available diesel fuel sample was analyzed with a JEOL JMS-T200GC equipped with a Zoex ZX-2 thermal modulator and GC Image software (version 2.5.0a2).

Results

The Kendrick mass scale that defines the mass of CH_2 as exactly 14.0000 is used to identify families of compounds that differ only by the length of alkyl substituents. The Kendrick mass is calculated as follows:

$$\text{Kendrick Mass} = \text{IUPAC mass} \times (14.00000/14.01565)$$

The Kendrick Mass Defect (KMD) is the difference between nominal Kendrick mass and exact Kendrick mass. The KMD is defined as follows on the GC Image software:

$$\text{Kendrick Mass Defect (KMD)} = \text{Kendrick Mass} - \text{nominal Kendrick Mass}$$

In a KMD plot, the Kendrick mass is used for the X-axis and KMD is used for the Y-axis. From left-to-right, the number of CH_2 units increases for the observed ions. From top-to-bottom, the differences in chemical formula such as the degree of unsaturation, oxidation, etc., increase. Families of homologous compounds are easily recognized in the KMD plot. A KMD plot was created for the composite mass spectrum created by summing all mass spectra in the GCxGC/FI analysis of the diesel fuel sample (Figure 2). Extracted ion current chromatograms (Figure 3) were created for compound families shown in Figure 2c.

Conclusion

Kendrick Mass Defect plots are a powerful tool for data analysis when combined with GCxGC/FI and high-resolution mass spectra measured with a JEOL JMS-T200GC system.

Table 1. Measurement condition.

| Condition	GC x GC/FI
Sample	Diesel Fuel
Concentration	1/100 (Hexane)
GCxGC system	ZX-2 thermal modulator (ZOEX Corp.)
1st column	Rxi-5SilMS, 30 m x 0.25 mm, 0.25 mm
2nd column	Rxi-17SilMS, 2 m x 0.15 mm, 0.15 mm
Modulation loop	Deactivated fused silica, 1.5 m x 0.15 mm
Modulation period	10 sec
Hot jet temp.	270 °C
Inlet pressure	200 kPa at Oven temp. 50 °C (Constant flow mode)
Inlet temp.	280 °C
Inlet mode	Splitless
Oven temp.	50 °C (1 min) -> 3 °C/min -> 280 °C (0.3 min)
GC-HRTOFMS system	JMS-T200GC (JEOL Ltd.)
Ion source	EI/FI/FD combination
Ionization mode	FI+
m/z range	m/z 35-500
Acquisition speed	33 spectra/sec
Software	GC Image™ Version 2.5.0a2
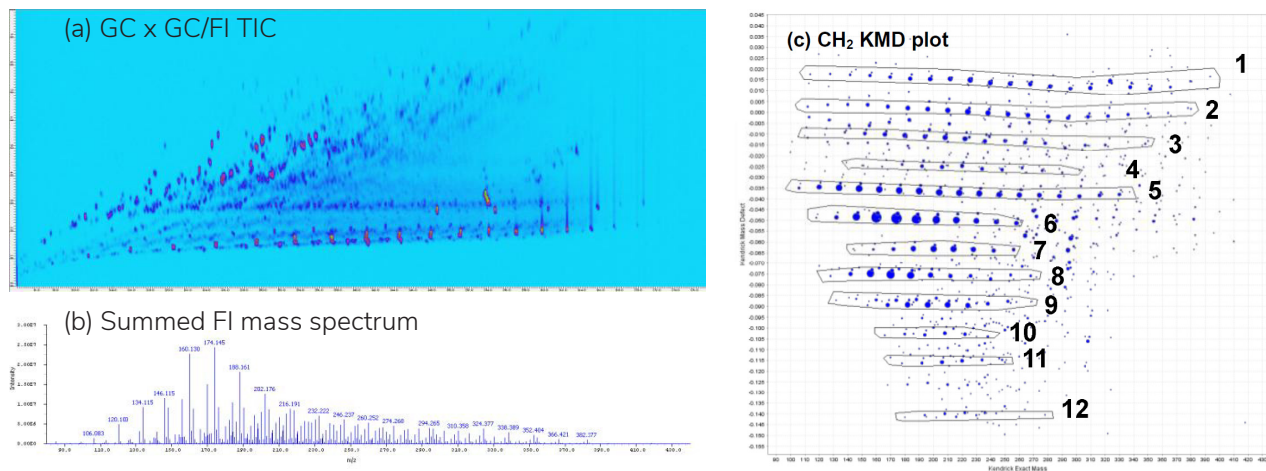
Figure 2. (a) 2-dimensional TIC chromatogram of the diesel sample, (b) the summed FI mass spectrum for the entire retention time region, (c) CH₂ Kendrick Mass Defect plot for the summed FI mass spectrum
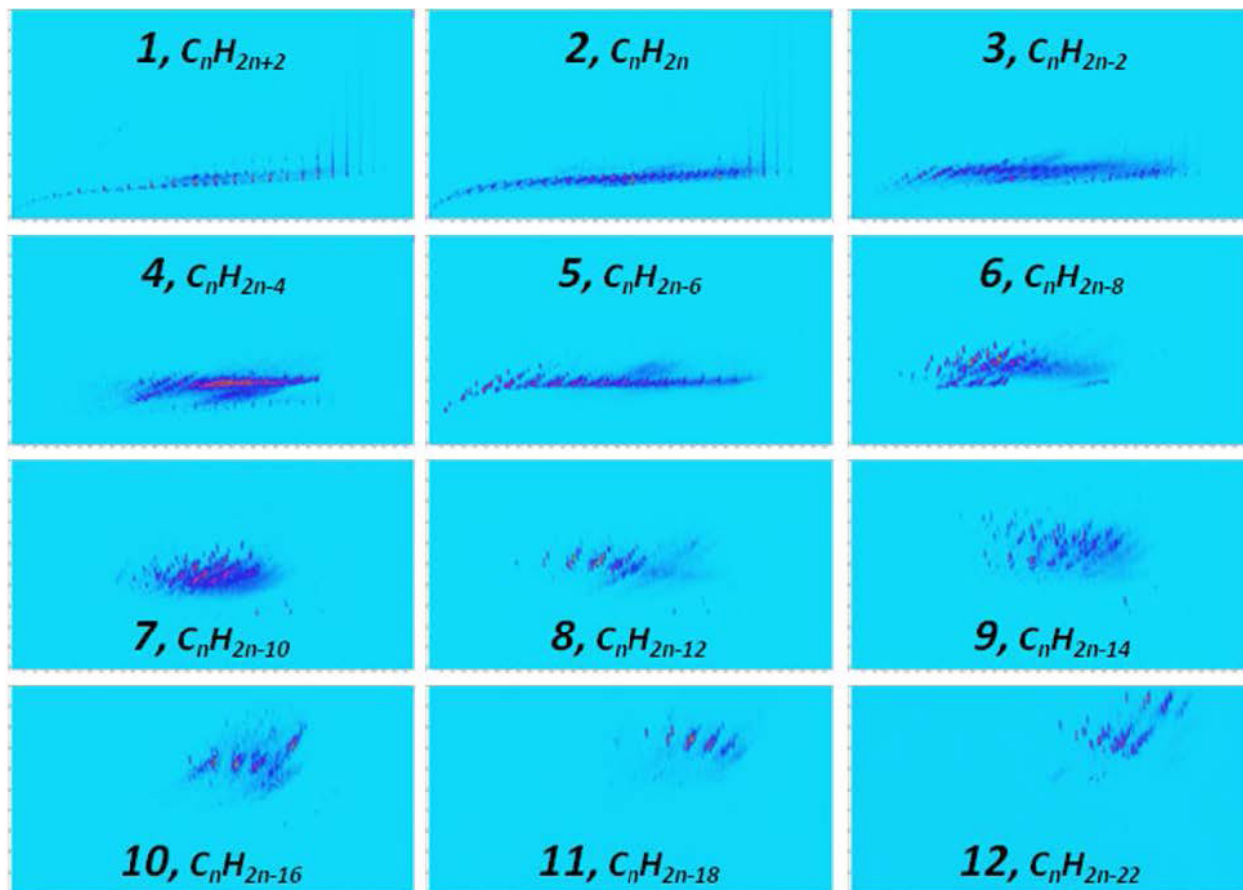
Figure 3. 2-dimensional SIC chromatograms using Kendrick m/z (in Figure 2) ± 0.015u