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GC-MS GCMS-QP™2050

Application News

Comprehensive Characterization of Diesel Fuel on GC×GC Utilizing Impressive High-Speed Scan Technology of GCMS-QP2050

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User Benefits

- Comprehensive characterization of complex matrices such as diesel fuel is possible with 2D gas chromatography.
- The impressive high-speed scan technology of GCMS-QP2050 allows for effective peak separation.
- Intuitive comprehension of compounds distribution can be achieved with displaying the data in a two-dimensional image.

■ Introduction

Kerosene, diesel, and other petroleum products are mixtures containing over 100 different hydrocarbons. The properties of petroleum products, such as ignitability and viscosity, depend on their composition and greatly affect physical properties like combustion. Comprehensive two-dimensional gas chromatography (GC×GC) offers high separation performance by utilizing two different columns, which provides more reliable compositional information for complex mixtures compared to one-dimensional chromatography. In this application, qualitative analysis of diesel fuel using a GC×GC system with GCMS-QP2050 that is capable of high-speed scanning (30,000 u/sec) was conducted. No less than 30,000 u/sec scanning speed improved the separation of peaks that are too close to each other and enabled accurate identification of compounds.

Fig. 1 GC×GC-MS System
(GCMS-QP™2050 and Nexis™ GC-2030)

■ System Configuration and Analysis Conditions

The system configuration and analysis conditions are shown in Table 1 and 2, respectively. GCMS-QP2050 equipped with a GC × GC thermal modulator (Zoex Corp., Houston, TX, USA) was used for the analysis. The capillary column set was the combination of the 15 m first column and 2.5 m second column (1.5 m: modulator loop section, 1 m: separation section). This modulator, cooled by liquid nitrogen, comprises a continuous cold jet gas and intermittently injected hot jet gas, enabling highly reliable thermal modulation. This facilitates band compression of analytes (Double Cryo-Focusing) and increase in sensitivity even for compounds with low boiling point (see Fig. 2 and 3).

Table 1 System Configuration

GC Model	: Nexis GC-2030 / AOC™-30i
MS Model	: GCMS-QP2050 (TMP exhaust: 255 L/sec)
Injection Port	: SPL
1st Column	: SH-1 (P/N : 227-36098-01) (15 m × 0.25 mm I.D., df= 1.0 µm)
2nd Column	: SH-Wax (P/N : 227-36356-01) (20 m × 0.1 mm I.D., df= 0.1 µm) *cut the column into 2.5 m
Modulator	: ZX1 thermal modulator(ZOEX corp.)
Nitrogen generator	: MT-24F (System Instruments Co., Ltd.)
Software	: Labsolutions™ GCMS GC Image (GC Image, LLC)
Library	: NIST Mass Spectral Library

Table 2 Analysis Conditions

GC	
Injection Temperature	: 275℃
Flow Control Mode	: Pressure (He)
Inlet pressure Program	: 150 kPa → 1.4 kPa/min → 300 kPa (13 min)
Purge Flow	: 10 mL/min
Injection Volume	: 0.2 µL
Split ratio	: 100
Column Oven Temp. Program	: 40℃ → 2.5℃/min → 240℃ (40 min)
MS	
Ion Source Temperature	: 200℃
Interface Temperature	: 240℃
Measurement Mode	: Scan
Scan Range (*m/z*)	: 35-500
Event Time	: 0.02 s (= 50 Hz、 30,000 u/sec)
Modulator	
Modulation period	: 5 s
Hot pulse duration	: 350 ms (300℃)
Cold Gas Flow	: 10 L/min (N_2)

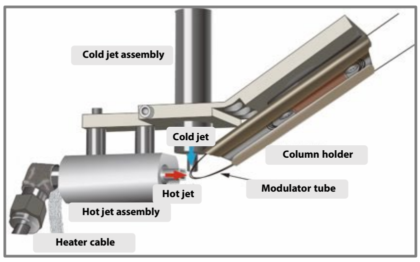

Fig. 2 ZX1 Thermal Modulator

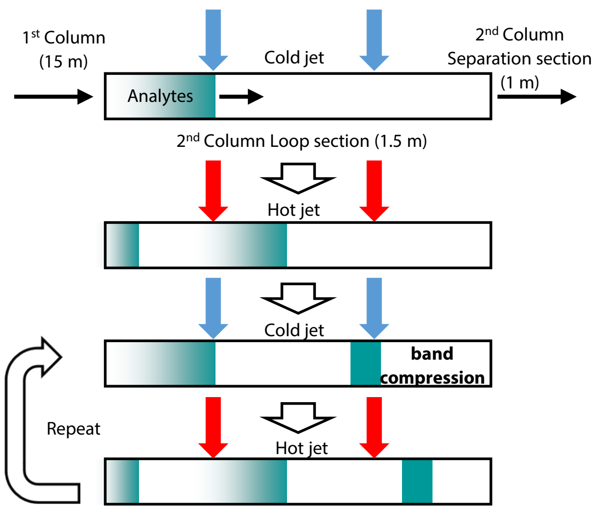

Fig. 3 Schematic illustration of the modulation process

■ Influence of Scan Speed

In GC×GC system, modulation contributes to high sensitivity analysis compared to one-dimensional gas chromatography. However, if scan speed is not sufficiently high, intervals of data points on chromatogram (event time) widen, leading to poor separation of peaks that are too close to each other (see Fig. 4). Therefore, by using high-speed scanning at 30,000 u/sec, it becomes possible to build an analysis system with high sensitivity and high resolution.

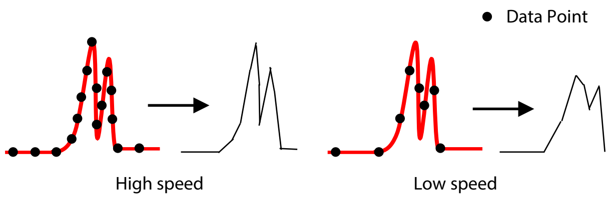

Fig. 4 Chromatograms with different Scan speed

■ Analysis of Diesel Fuel

The diesel sample was injected with 0.2 µL of the original solution without performing pre-injection solvent wash to avoid affecting the composition of the sample. The two-dimensional image obtained using the GC Image software (GC Image, LLC) is shown in Fig. 5. It was observed that a lot of peaks in the form of blobs appeared. The horizontal axis corresponds to the separation on the first column, while the vertical axis corresponds to the separation on the second column. In the case of using a non-polar column for the first column and a highly polar column for the second column in this study, the horizontal axis corresponded to boiling point and the vertical axis corresponded to polarity. As a result, a two-dimensional image was obtained where the components of aliphatic and aromatic compounds were specifically distributed based on the boiling point and polarity of the compounds. Additionally, aromatic compounds could be clearly separated based on the number of aromatic rings.

■ Evaluation of Impact of the Modulator

To evaluate effect of the modulator in GC×GC, a comparison was made with 1D GC-MS for 6-Methyltetraline shown in Figure 5. The column used for 1D GC-MS was the same as the first column in GC×GC, SH-1 (15 m × 0.25 mm I.D., df= 1.0 µm). A part of the chromatogram and the results of similarity search are shown in Fig. 6.

In the TIC chromatogram of 1D GC-MS, the peak of 6-Methyltetraline containing m/z 146 was hardly detected due to the influence of the other compounds. As a result, the similarity score in mass spectra was low(72). On the other hand, in GC×GC-MS, it was observed that the peak width was approximately 0.2 seconds, very sharp, and the peak intensity was high. Furthermore, it was completely separated from aliphatic compounds containing the m/z 85 and 2-Methylnaphtalene containing the m/z 141, with a high similarity score (94) in the mass spectra, matching 6-Methyltetraline (Fig. 6, 7).

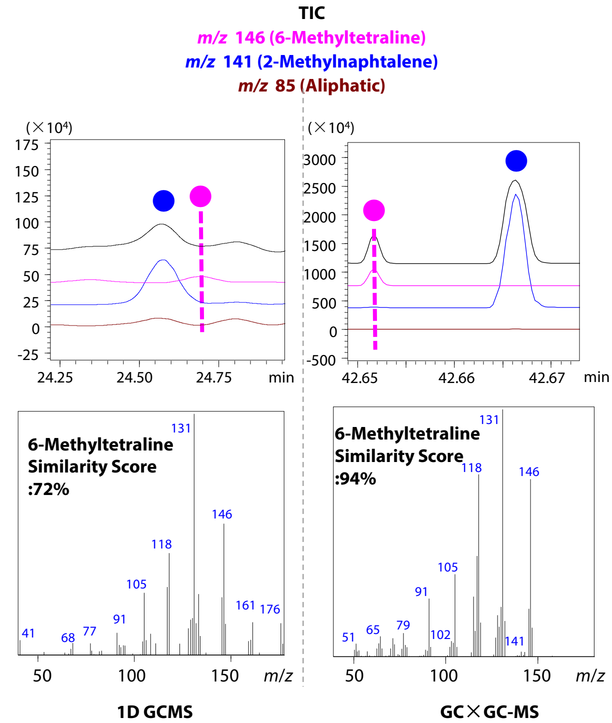

Fig. 6 Comparison of 1D GCMS and GC×GC-MS

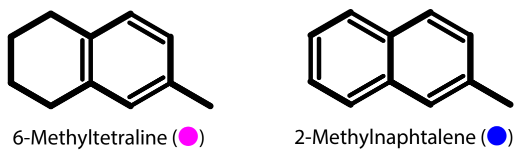

Fig. 7 Structural formula of 6-Methyltetraline and 2-Methylnaphtalene

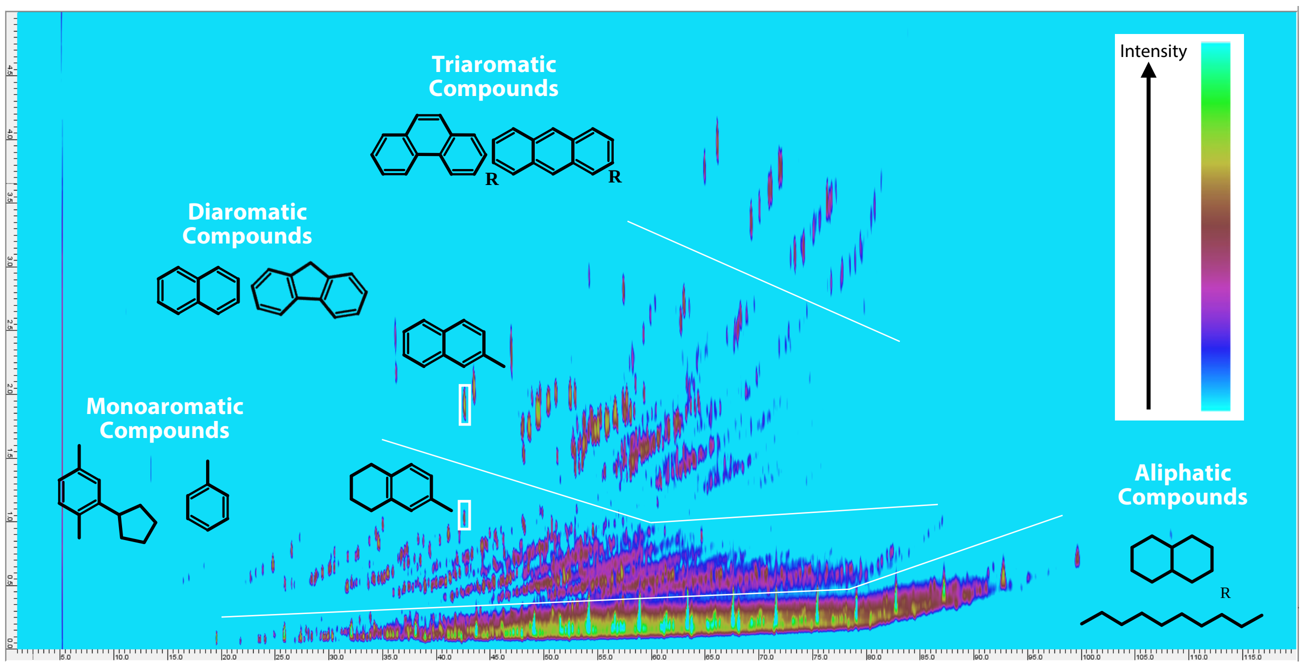

Fig. 5 TIC two-dimensional plot of the analysis of a diesel sample

■ Influence of Scan Speed

To evaluate difference of scan speed, measurements were carried out at scan speeds of 15,000 u/sec (25 Hz) and 30,000 u/sec (50 Hz). Chromatograms of three aromatic compounds (A-C) each with fragment ions m/z 162, 148, and 146 are showed in Fig. 8. In the one-dimensional TIC chromatogram, at 15,000 u/sec, 9 points were drawn in the range containing compounds B and C, while at 30,000 u/sec, 18 points were drawn, indicating better separation of B and C. As a result, in the two-dimensional image, the separation of blobs and contrast became better at 30,000 u/sec. Thus, high-speed scanning enables achieving excellent separation even for peaks which are too close.

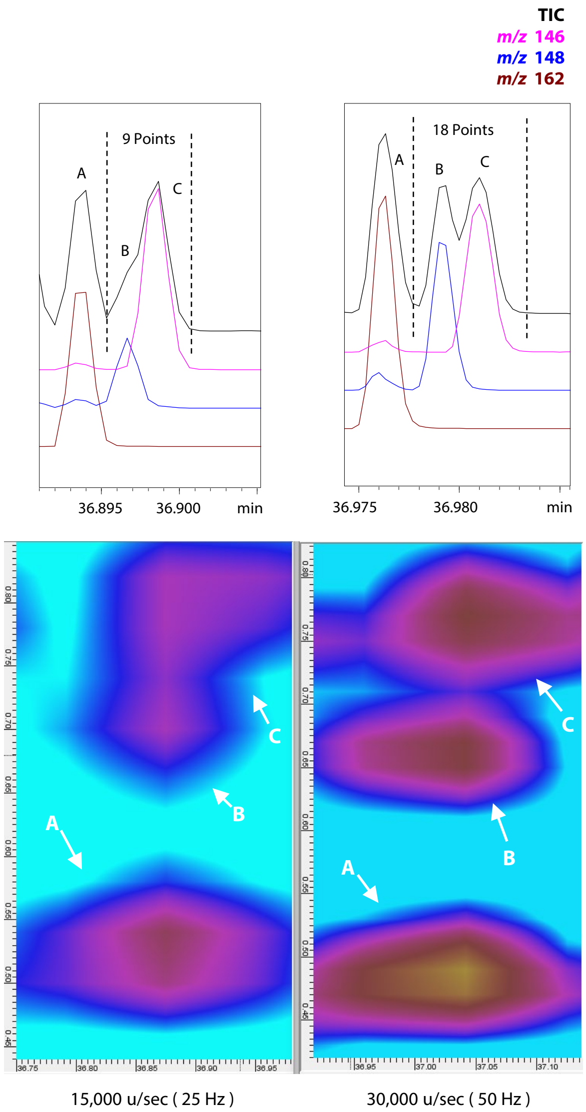

Fig. 8 Comparison of Scan Speed

■ Conclusion

Diesel, a complex mixture of hydrocarbons, was measured using GC×GC-MS. Each component on the two-dimensional image showed characteristic distribution based on its molecular structure, allowing for intuitively understanding of the composition of diesel. Additionally, GC×GC-MS demonstrated Excellent separation performance for components, enabling more reliable identification of components of diesel compared to 1D GC-MS. The high-speed scan of GCMS-QP2050 (30,000 u/sec) contributes to more precise qualification analysis.

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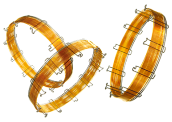

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