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The analysis of olefine and aromatic hydrocarbon in hydrocarbon mixture using Multi-Dimensional GC/GCMS system

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Introduction

The component of hydrocarbon mixture is very complicated, including even and odd number carbon hydrocarbon. Its analysis with conventional gas chromatographic approaches is a big challenge and can give us inaccurate or even false results because overlapping is always happened. Many measures were taken to avoid interferences, such as improving sample preparation or using high selectivity detectors. Multi-dimensional GC/GCMS system with multiple heart-cutting is one of the powerful tools. Multi-dimensional GC/GCMS can improve resolution beyond that of the regular GC analysis as it re-introduces the dissolved component of interest into another column. In other words, only part of the peak of the component that was insufficiently separated on the column where the sample initially passed through (called the "1st column") is introduced (heart-cut) to a column of another type (called the "2nd column"), so that insufficiently separated components can be separated. A device called a "switching device" is used for heart-cut introduction of peaks eluted from the 1st column to the 2nd column. As a switching device, the recently developed Multi-Deans switching unit can be used in combination with a GC-FID as the first analytical dimension and a GCMS as the second analytical dimension. The analytes pass the first column and are detected in the FID ("stand-by mode") or are transferred to the second column and analyzed with mass spectrometer or GC detector such as FID ("cut mode"). By using this system, complicated matrix analysis such as hydrocarbon mixture was done to demonstrate MDGC/GCMS system performance.

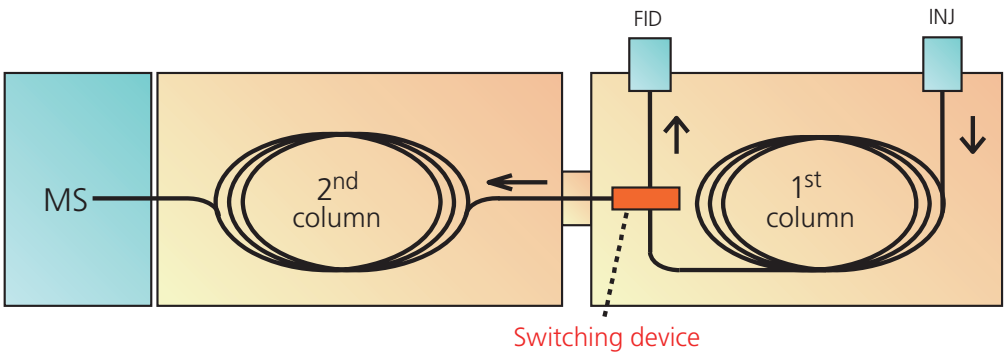

Fig. 1 Multidimensional GC/GCMS system

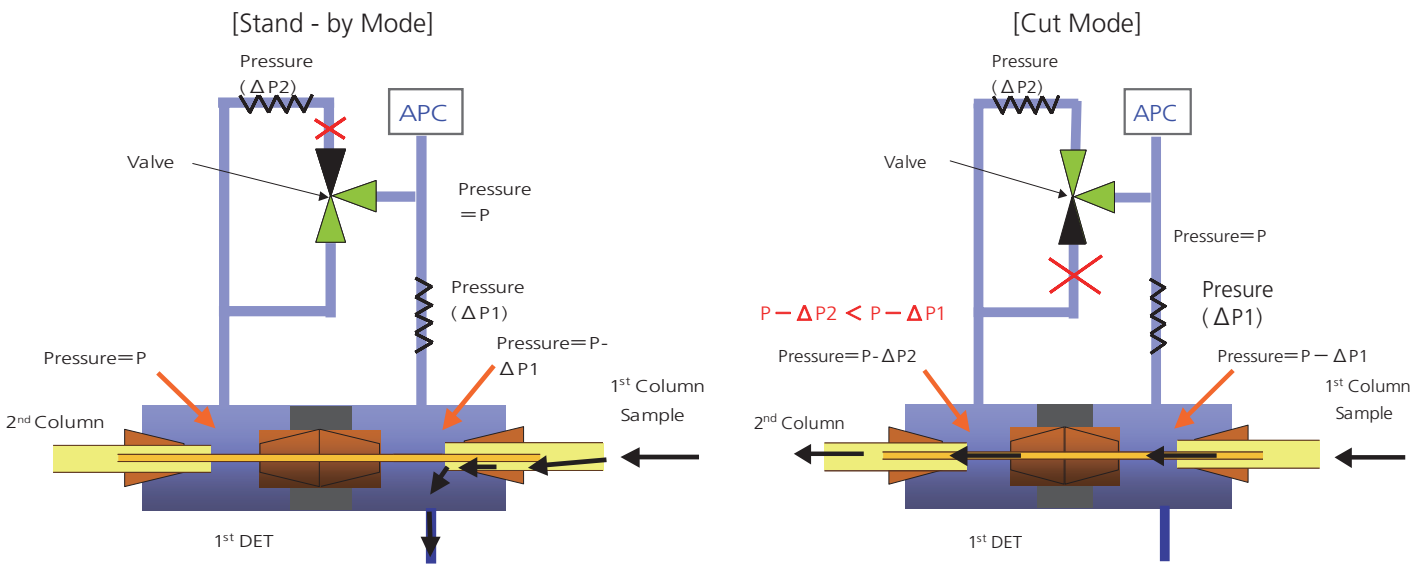

Fig. 2 Schematic diagram of the Multi-Deans switching device

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Instrumentation and operational conditions

The Shimadzu MDGC system consisted of two GC-2010 gas chromatographs (defined as GC 1 and GC 2), an MS-QP2010 quadrupole mass spectrometer with an AOC-20i autosampler (Shimadzu Corporation, Kyoto, Japan).
One-dimensional GC analytical conditions: Inlet: 280°C; Injection mode: split (split ratio 50); Injection volume: 0.2 ul; Carrier gas: helium; Carrier gas control: constant pressure 186.7 kPa; Column 1: HP-1 (30 m × 0.25 mm × 0.25 um) Column temperature:60°C (3 min) 10°C / min 170°C 1°C / min 205°C 10°C / min 290°C (10 min) FID temperature: 300°C; Hydrogen flow rate: 40 ml / min; Air flow rate: 400 mL / min; Makeup gas (He) flow rate: 5 mL / min; Switching pressure:121.1 kPa ;
Two-dimensional GCMS analytical conditions: Column 2: Rtx-2330 (60 m × 0.32 mm × 0.2 um) Ion source temperature: 200°C; Interface temperature: 230°C; Scan Mode: SCAN; Scan range: 35-400 *m/z*;
Cutting program: Cutting C17 non-normal alkane (22.99-26.06 min; 26.68-27.99 min) Cutting C18 non-normal alkane (28.03-30.66 min; 31.71-32.90 min) Cutting C19 non-normal alkane (32.91-36.03 min; 37.00-38.47 min) Cutting C20 non-normal alkane (38.52-42.24 min; 42.95-50.00 min)
Column 2 temperature-programmed condition when cutting C17 non-normal alkane:
40°C (3 min) 3°C/min 100°C (10 min) 10°C/min 210°C (10min)
Column 2 temperature-programmed condition when cutting C18 non-normal alkane:
40°C (3 min) 3°C/min 100°C (6 min) 0.5°C/min 110°C 10°C/min 220°C (10 min)
Column 2 temperature-programmed condition when cutting C19 non-normal alkane :
40°C (3 min) 2°C/min 110°C (10 min) 5°C/min 140°C 10°C/min 230°C (10 min)
Column 2 temperature-programmed condition when cutting C20 non-normal alkane:
40°C (3 min) 2°C/min 110°C (10 min) 5°C/min 140°C 10°C/min 230°C (10 min)

Results and Discussion

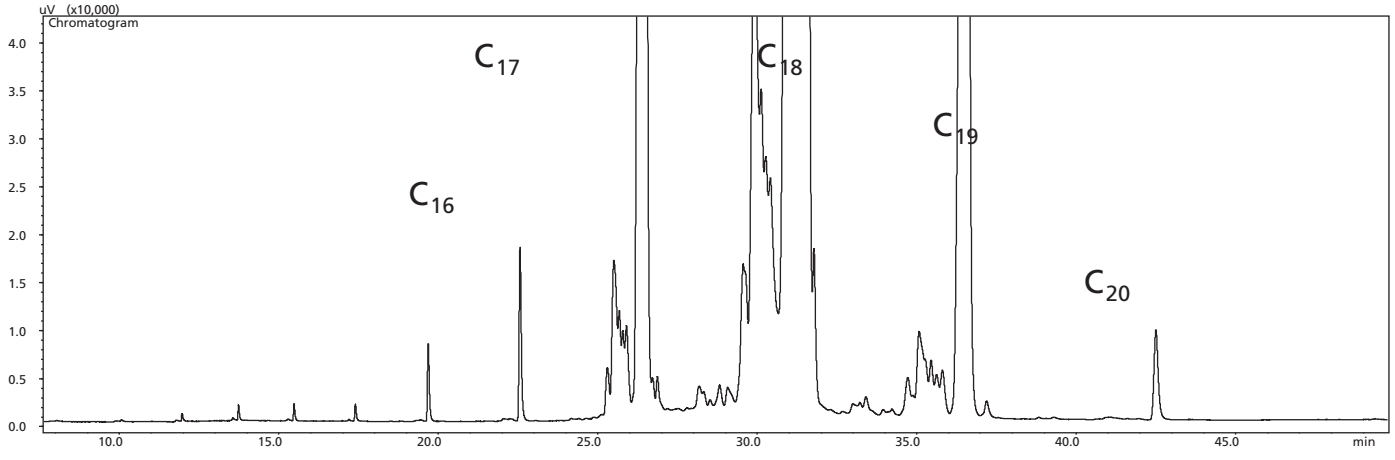

Fig. 3 Not cutting, one-dimensional GC spectrum.

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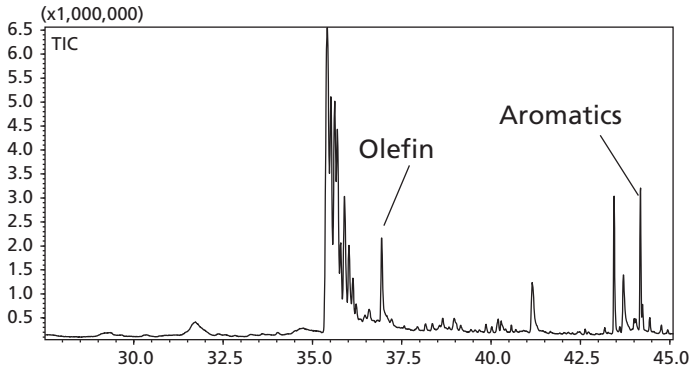

Fig. 4 Two-dimensional GCMS spectrum of cutting C_{17} non-normal alkane (22.99-26.06 min; 26.68-27.99 min).

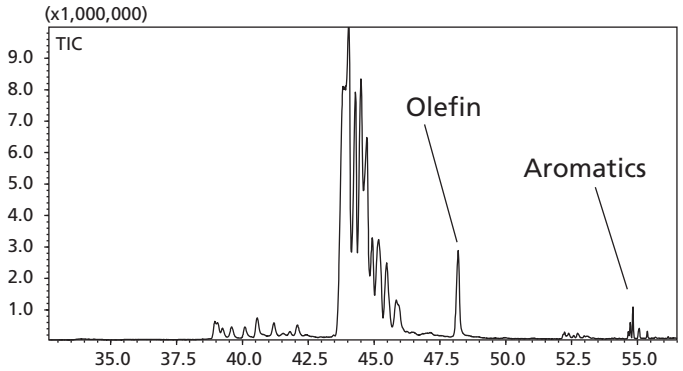

Fig. 5 Two-dimensional GCMS spectrum of cutting C_{18} non-normal alkane (28.03-30.66 min; 31.71-32.90 min).

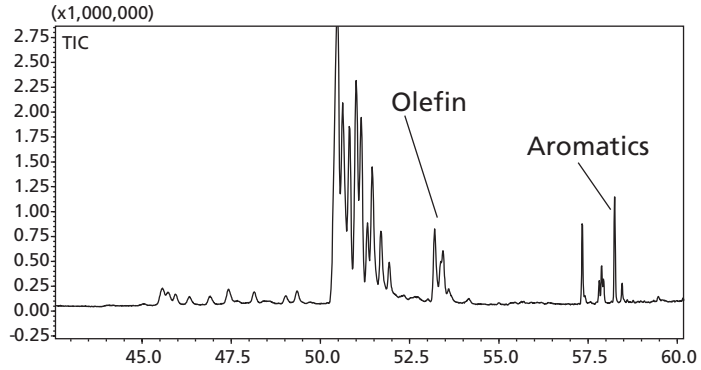

Fig. 6 Two-dimensional GCMS spectrum of cutting C_{19} non-normal alkane (32.91-36.03 min; 37.00-38.47 min).

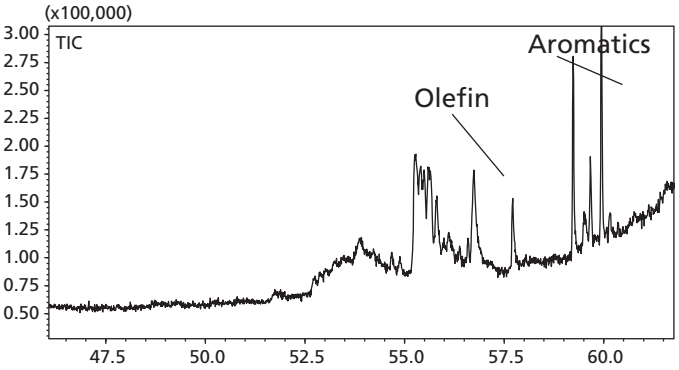

Fig. 7 Two-dimensional GCMS spectrum of cutting C_{20} non-normal alkane (38.52-42.24 min; 42.95-50.00 min).

The quantitative results are based on the area normalization method, the total content of the isomerization, olefins and aromatics with same carbon numbers is calculated with the one-dimensional result; the percentage of the isomerization, olefins and aromatics is calculated respectively with the two-dimensional result. The result show that the total content of olefin is 6.64%, the total content of aromatic is 0.67%.

Conclusion

This MDGC/GCMS system can analyze the olefine and aromatic hydrocarbon in hydrocarbon mixture. It has superiority on the determination of the complicated matrix sample in order to obtain more reliable analytical results.

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