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Application News

GC-MS GCMS-TQ™8040 NX

Analysis of Double Bond Position in Olefins by Solvent-Mediated Chemical Ionization (SMCI)

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User Benefits

- Chemical ionization can be used without using a high-pressure cylinder of flammable gas.
- The specific ion can be monitored by attaching a reaction ion from acetonitrile to double bond in carbon chain.
- Furthermore, the position of those double bonds can be analyzed from product ion scans obtained by GC-MS/MS.

■ Introduction

Olefins are unsaturated hydrocarbons with one carbon-carbon double bond and are used as an ingredient in a variety of materials and paints. Moreover, they are a class of compounds generated from chemical recycling that has attracted attention in recent years.

They need to be analyzed because the chemical properties of such olefins differ depending not only on the number of carbon atoms, but also the double bond position. Chromatography requires using standard solutions, but they are not available for all compounds. Therefore, this article describes a technique for analyzing the double bond position in olefins based on mass spectra obtained with a GC-MS/MS using solvent-mediated chemical ionization (SMCI).

■ Measurement Sample

A standard solution of 8 olefins was prepared with 50 µg/mL of each compound.

■ Analytical Conditions

Table 1 Instruments Used and Analytical Conditions

Instrument Used	
GCMS:	GCMS-TQ8040 NX
Autosampler:	AOC-20i+s Plus
Column:	SH-I-5MS (30 m x 0.25 mm I.D., df = 0.25 µm)
Insert Liner:	Split-less Deactivated Liner w/ Low Wool
GC Conditions	
Injection Unit Temp.:	250 °C
Injection Volume:	1 µL
Injection Mode:	Splitless
Carrier Gas Control:	Linear velocity (42.5 cm/sec)
Column Oven Temp.:	60 °C (1 min) → (15 °C/min) → 300 °C (3 min)
MS Conditions	
Interface Temp.:	250 °C
Ion Source Temp.:	200 °C
Ionization Method:	SMCI (acetonitrile)
Measurement Mode:	Scan and product ion scan (CE = 2 V)
m/z Measurement Range:	50 - 300

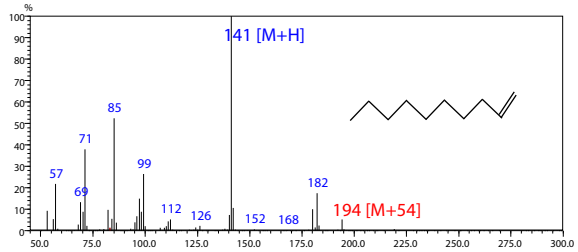
Fig. 1 SMCI Unit (Left) and GCMS-TQ8040 NX (Right)

■ Analysis Results

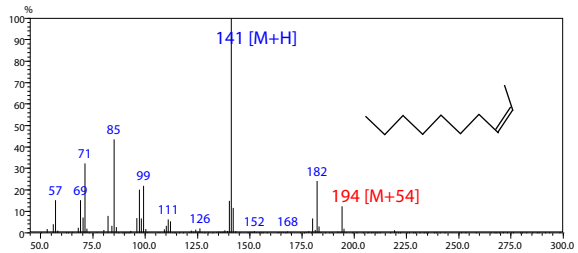
• Confirming Adduct Ions in the Scan Mode

First, the base peak confirmed at [M + H] (*m/z* 141) was used to determine the carbon chain length based on the molecular weight. If acetonitrile is used for SMCI, then (1-methyleneimino)-1-ethenylium (MIE) is formed at *m/z* 54 inside the ion source as a reaction ion for the double bond. With the scan mode, the [M + 54] (*m/z* 194) ion with MIE adducted to the double bond can be confirmed together with other ions (Fig. 2). Checking for this [M + 54] ion can confirm the presence of a carbon-carbon double bond. However, although the mass spectra of compounds with different double bond positions are shown in Fig. 2, it is not possible to determine the positions of these bonds. Therefore, next a product ion scan is performed with the [M + 54] ion as a precursor ion.

1-Decene



2-Decene



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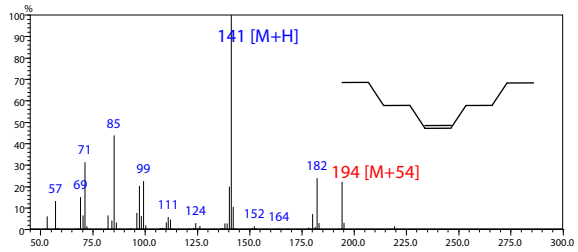
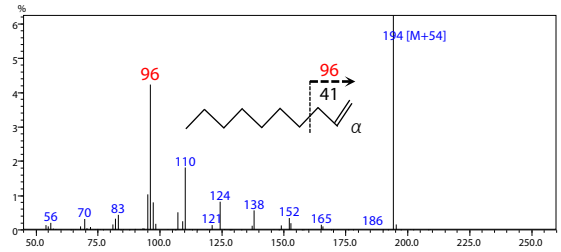


Fig. 2 Mass Spectra Obtained by Scan Mode Analysis

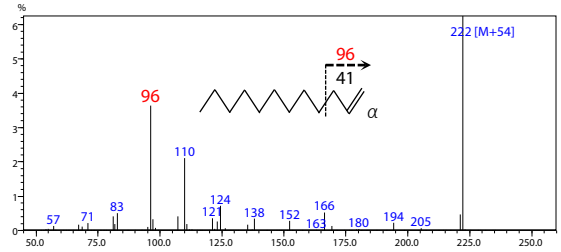
• Analysis of the Double Bond Position Based on Product Ion Scans

The product ion scan mass spectra for the different olefin types are shown below. α, β, and γ olefins include a double bond at a terminus, which generates identical product ions that do not differ depending on the carbon chain length (Fig. 3). For these three types, the double bond position can be determined from *m/z* values 96, 110, and 124.

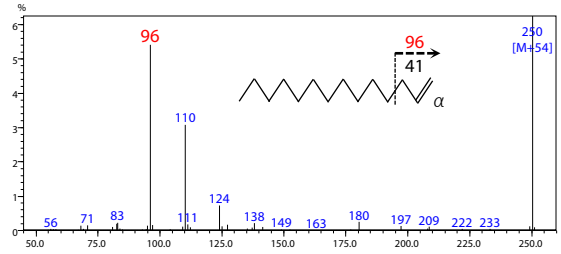
1-Decene



1-Dodecene



1-Tetradecene



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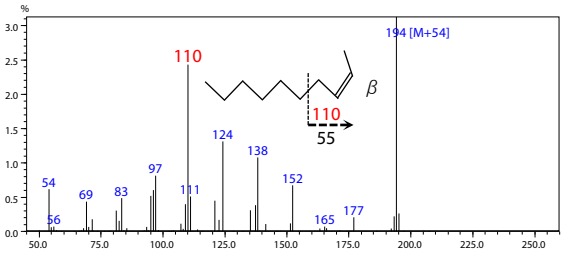


3-Dodecene

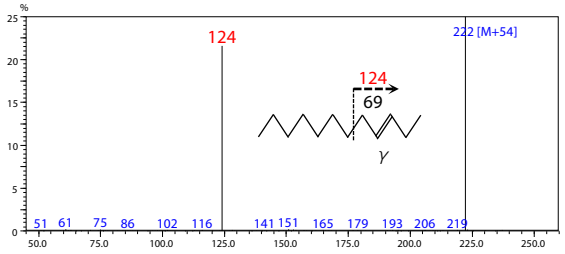
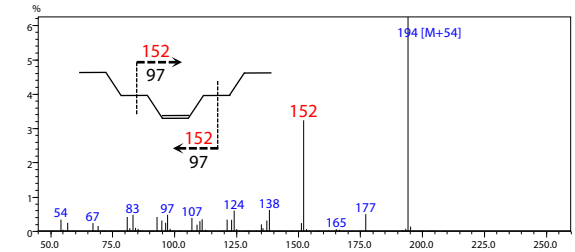


Fig. 3 Product Ion Scan Mass Spectra for α, β, and γ-Olefins

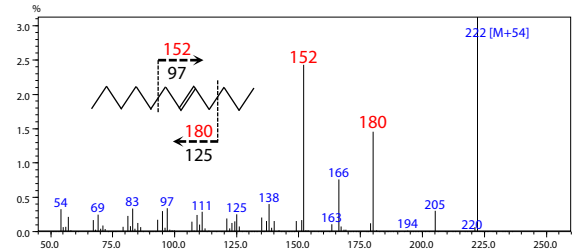
For other olefins, the double bond position can be determined from the 1 or 2 type-specific ions that can be confirmed in the product ion scan for [M + 54] (Fig. 4). This is because MIE can be adducted in two orientations with respect to the double bond, which generates two types of fragmentation depending on the orientation.[1)]

The arrows indicated on each structural formula show the fragment that can be confirmed in mass spectra. The red numbers indicate the *m/z* value where the fragments with MIE ion adducted can be confirmed with a product ion scan. The black numbers indicate the molecular weight of the fragment without the adduct ion.

5-Decene



5-Dodecene



7-Tetradecene

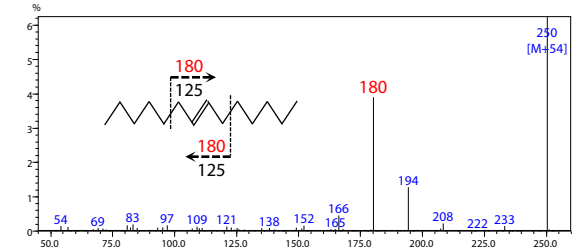


Fig. 4 Product Ion Scan Mass Spectra for Other Olefins

■ Conclusion

SMCI enables chemical ionization without flammable gases.
In addition to confirming molecular weight information, SMCI can also be used in combination with GC-MS/MS to determine the position of double bonds in carbon chains. This is especially useful for analyzing the structures of compounds for which standard samples are difficult to obtain.

Reference
1) Van Pelt, C.K. and J.T. Brenna, *Anal Chem*, 1999. **71**(10): p. 1981-9.

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