

Application News

No. M270

Gas Chromatography Mass Spectrometry

Analysis of Hydrocarbons Using PCI-GC-MS

Interest in hydrocarbon-producing microalgae is growing in the field of renewable energy development. Since the hydrocarbons produced by microalgae contain no oxygen and are similar in properties to heavy oil, they can be a convenient substitution for existing liquid fuels, and it is advantageous that an energy resource do not compete with food production. Research is being performed into obtaining petrochemical raw material from the hydrocarbons produced by microalgae, and mass spectrometry is used in identification of these products.

Gas chromatography-mass spectrometry (GC-MS) normally uses electron ionization (EI) to produce ions for analysis, but when using this EI method for hydrocarbon analysis, the larger the carbon number the more difficult it becomes to confirm the molecular ions on a mass spectrum. The ion-molecule reactions that occur with positive chemical ionization (PCI), however, tend to produce protonated molecules and dehydride molecules, from which information about molecular mass is easier to obtain compared to the EI method.

In this article, we describe a case example of using PCI-GC-MS to measure hydrocarbons obtained from the catalytic decomposition of squalane, a compound obtained from microalgae.

Table 1 Analytical Conditions

Shimadzu Gas Chromatograph	
Mass Spectrometer	: GCMS-QP2010 Ultra
GC	
Column	: Rtx®-1 PONA (Shimadzu GLC Ltd.: P/N 314-100) 100 m × 0.25 mm I.D., 0.5 µm
Carrier Gas	: He
Control Mode	: Linear Velocity (21.2 cm/sec)
Injection Mode	: Split
Split Ratio	: 26.8
Oven Temperature	: 40 °C (10 min) → 3 °C/min → 300 °C (45 min)
Sample Injection Volume	: 1.0 µL (2.0 µL for the PCI method)
MS (EI Method)	
Ion Source Temperature	: 200 °C
Interface Temperature	: 300 °C
Tuning Mode	: High concentration
Measurement Mode	: Scan (<i>m/z</i> 10 to 500)
Event Time	: 0.3 sec
Ionization Voltage	: 70 V
MS (PCI Method)	
Reagent Gas	: Methane
Ion Source Temperature	: 170 °C
Interface Temperature	: 300 °C
Tuning Mode	: Standard
Measurement Mode	: Scan (<i>m/z</i> 45 to 500)
Event Time	: 0.3 sec
Ionization Voltage	: 70 V

■ Sample

Squalane was decomposed using a catalyst, the products of decomposition were diluted in mesitylene solvent, and this sample was analyzed using GC-MS. The sample was provided by Prof. Keiichi Tomishige, Department of Applied Chemistry, Graduate School of Engineering, Tohoku University.

■ Analytical Conditions

Analysis was performed using both the EI method and the PCI method of ionization. For analysis by the PCI method, a specialized PCI ion source was used with methane as the reagent gas. For both the PCI method and the EI method, process conditions were optimized automatically by autotuning before performing analysis. Analytical conditions are shown in detail in Table 1.

Results

Total ion current chromatograms (TICC) by the EI method and the PCI method are shown in Fig. 1 and 2, respectively. Mass spectra of peaks (1) and (2) (fractions corrected for hydrogen containing compounds) are shown in Fig. 3 to 6. The peak at 108 on the chromatograms is squalane ($C_{30}H_{62}$). Determining the maximum m/z on the EI mass spectra is difficult (Fig. 3 and 5), while peaks at m/z 281 and 337 can be observed on the PCI mass spectra (Fig. 4 and 6). Analyzing hydrocarbons using the PCI method also normally results

in dehydride molecules. Assuming 282 and 338 were molecular masses, we checked the difference to the second largest m/z and found there was difference of 15 in both cases (cleavage of a methyl group), showing the results were appropriate. Finally, the carbon number was estimated based on the ratio of the maximum m/z and the peaks plus one (282/281 and 338/337) and the isotopic ratio of carbon, where peak (1) was assumed to be $C_{20}H_{42}$ (molecular mass: 282) and peak (2) was assumed to be $C_{24}H_{50}$ (molecular mass: 338).

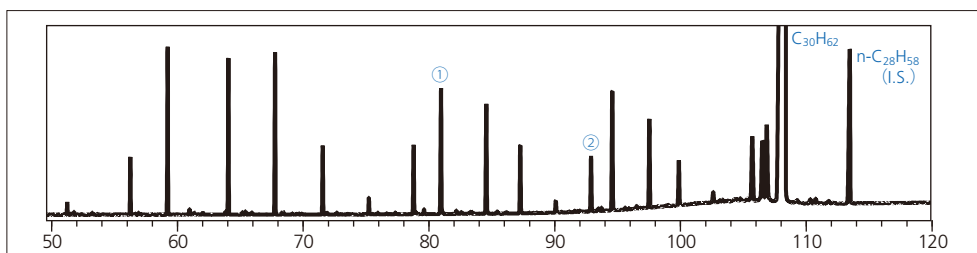


Fig. 1 Total Ion Current Chromatogram (EI)

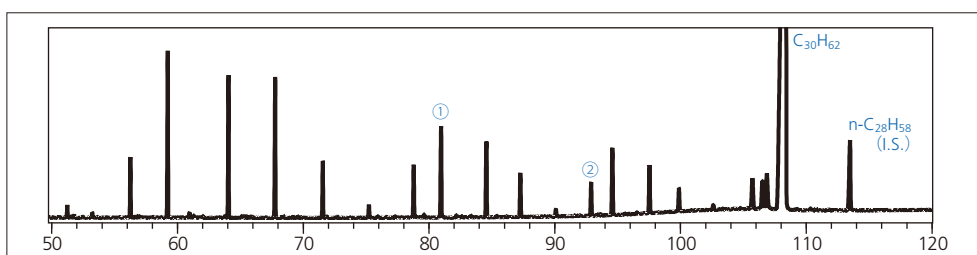


Fig. 2 Total Ion Current Chromatogram (PCI)

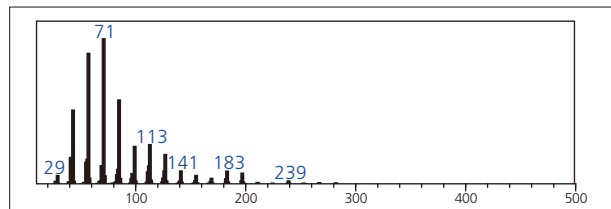


Fig. 3 Mass Spectrum (peak (1), EI)

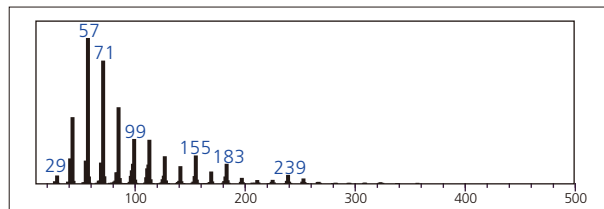


Fig. 5 Mass Spectrum (peak (2), EI)

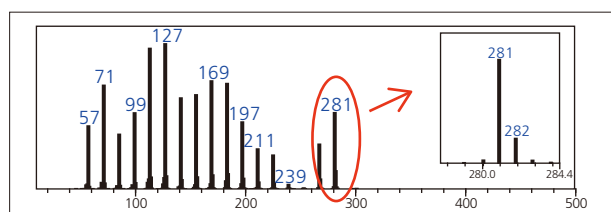


Fig. 4 Mass Spectrum (peak (1), PCI)

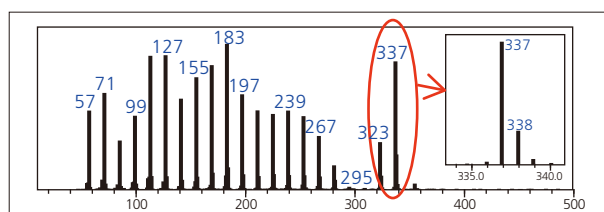


Fig. 6 Mass Spectrum (peak (2), PCI)

Conclusions

We were able to obtain information on the molecular mass of hydrocarbons using PCI-GC-MS. PCI analysis was made easy using the GCMS-QP2010 Ultra due to the use of a special PCI ion source and process condition optimization by autotuning.

References

Catalytic Production of Branched Small Alkanes from Biohydrocarbons
Shin-ichi Oya, Daisuke Kanno, Dr. Hideo Watanabe, Dr. Masazumi Tamura, Dr. Yoshinao Nakagawa and Prof. Dr. Keiichi Tomishige,
Article first published online: 11 JUN 2015, DOI: 10. 1002/cssc. 201500375

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