

Isotopologue analysis of Polycyclic Aromatic Hydrocarbon (PAH) using APCI-Orbitrap MS and NMR

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Polycyclic aromatic hydrocarbons (PAHs) are widely distributed in the petroleum, soil, ocean, atmosphere, and extraterrestrial materials. Especially PAHs can be extracted directly from sediments and/or hydrothermal pyrolysis of sediment organic matter, including highly matured kerogen [1-2]. The isotopologues (¹³C multiple and/or position-specific substituted) of PAHs may inform of modern and ancient carbon cycling, though stable isotope analysis of PAHs has been so far limited to bulk ¹³C/¹²C analysis through Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry (GC-C-IRMS) [3].

Here, we report method development of isotopologue analysis using high-mass-resolution Orbitrap mass spectrometer and Nuclear Magnetic Resonance (NMR). Commercial PAHs (anthracene, phenanthrene, pyrene, and fluoranthene) were introduced into the Orbitrap MS through Atmospheric Pressure Chemical Ionization (APCI). First, the mass species of each PAH—M0 (all ¹²C), M1 (single ¹³C substitution), M2 (double ¹³C substitution), and M3 (triple ¹³C substitution)—were measured simultaneously for ¹³C clumped isotope analysis. The isotope ratios were calculated based on the intensity of each mass peak: $^{13x1}R = I_{M1}/I_{M0}$, $^{13x2}R = I_{M2}/I_{M0}$, and $^{13x3}R = I_{M3}/I_{M0}$. Then, δ values defined as $\delta^{13xn}C = ((^{13xn}R_{\text{sample}} / ^{13xn}R_{\text{standard}}) - 1) \times 1000\text{‰}$, were calculated. We used dual syringe analysis of two different commercial PAHs as sample and standard, and calculate the clumped isotopologue abundance as $\Delta^{13x2}C = \delta^{13x2}C - 2\delta^{13x1}C$ and $\Delta^{13x3}C = \delta^{13x3}C - 3\delta^{13x1}C$, which represent relative difference of deviations from the stochastic distribution. Analytical precisions achieved range from 0.1‰ to 0.5‰ for $\delta^{13x1}C$, 0.06 to 1.3‰ for $\Delta^{13x2}C$, and 0.75‰ to 2.6‰ for $\Delta^{13x3}C$, when using a total sample amount of 17.5 nmol in 350 μ L. In addition, position specific isotope analysis (PSIA) was made using the higher-energy collisional dissociation (HCD) cell. The ion fragments from each PAH were produced by the collision and introduced into the Orbitrap mass analyzer. In the case of phenanthrene (C₁₄H₁₀), C₄ to C₁₄ fragments were identified, and their carbon isotope ratios were determined. These results were compared with independent analyses using ¹³C-NMR. The combined isotopologue analysis using both Orbitrap MS and ¹³C-NMR is useful to determine accurate clumped and position-specific isotopes within PAHs.

References

[1] Brocks et al. (2003), *Geochimica et Cosmochimica Acta*, 67(8), 1521-1530.

[2] Marshall et al. (2007), *Precambrian Research*, 155(1-2), 1-23.

[3] Norman et al. (1999), *Atmospheric Environment*, 33(17), 2807-2814.