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Poster Session Day 2

The ^{13}C-^{13}C clumping and PSIA of Polycyclic Aromatic Hydrocarbon (PAH) using ESI/APCI-Orbitrap Mass Spectrometry

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Polycyclic Aromatic Hydrocarbons (PAHs) can be obtained from hydropyrolysis of matured sedimentary organic matter [1-3], and thus has potential to provide additional information on ancient biogeochemical carbon cycling. Isotopic analysis of PAHs has been conducted using GC-C-IRMS [4]. Doubly ^{13}C substituted isotopologue analysis of PAHs using GC-Orbitrap has been performed for meteorite samples [5,6]. Higher precision and accuracy require repeated analysis of standard samples, though low vapor pressure of PAH prohibits stable introduction into gas-source mass using conventional dual inlet. Here, we developed a new method for measuring PAH isotopologues using an ESI/APCI-Orbitrap equipped with a dual syringe system. All analytical conditions including solutions, ionization and orbitrap analysis, were optimized. M0 (all ^{12}C), M1 (single ^{13}C substitution), M2 (double ^{13}C substitution), M3 (triple ^{13}C substitution) were separated by their precise mass, and isotope ratios were calculated from intensity of each mass spectrum (^{13}R=M1/M0, $^{13\text{-}13}R$=M2/M0, $^{13\text{-}13\text{-}13}R$=M3/M0). Clumped isotopologue abundance (Δ value) is defined by the deviation from equilibrium constant of the homogeneous isotope exchange reaction ($\Delta^{13}C^{13}C = \delta^{13}C^{13}C - 2\delta^{13}C$, $\Delta^{13}C^{13}C^{13}C = \delta^{13}C^{13}C^{13}C - 3\delta^{13}C$). The dual syringe analysis of two different reagents of four PAHs (anthracene, phenanthrene, pyrene, and fluoranthene) gave analytical precisions of 0.09-0.5‰ for $\delta^{13}C$, 0.06-1.3‰ for $\Delta^{13}C^{13}C$ and 0.8-2.6‰ for $\Delta^{13}C^{13}C^{13}C$ when using small samples (17.5 nmol/0.35 mL). These results suggest that isotopologue analysis using ESI/APCI-Orbitrap MS may be useful for the analysis of PAHs extracted from ancient sedimentary organic matter.

References

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