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Session 5b) Novel Methodology 2: Technical Development

Measuring intramolecular carbon isotope distributions in amino acids using Fourier transform mass spectrometry

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The measurement of intramolecular isotopic differences allows questions about the formation of molecules and their alteration by biological and abiotic processes to be explored. Until recently, intramolecular isotope measurements (i.e., position-specific isotope analysis, PSIA) were laborious, requiring large amounts of analyte and / or specialized instrumentation. Fourier transform mass spectrometers (FT-MS, i.e., Orbitrap™ mass spectrometry) fragment molecules with high mass resolution which allows differentiation between individual isotopologues (e.g., molecules with a single heavy isotope substitution like ^{13}C or ^{15}N) such that they can be resolved from one another and used to calculate isotope ratios on both the molecular average and position-specific levels. Here, we demonstrate the ability of this method to measure the molecular average and position-specific carbon isotope structure of the amino acid alanine using electrospray ionization FT-MS (ESI-FT-MS). Aliquots of alanine were labeled at each individual carbon position separately to permit linking specific atoms in fragments to the original molecular structure and detect any recombination of atoms in resultant fragments. Analyses include measurements of ^{13}C-labeled materials with molecular average carbon isotope values anchored to the Vienna Peedee Belemnite reference scale and position-specific carbon isotope compositions determined independently by gas source isotope ratio mass spectrometry. Isotope data from ESI-FT-MS agrees with gas source isotope ratio mass spectrometry measurements, giving further confidence to this novel approach to PSIA. The carbon isotope analyses by ESI-FT-MS were rapid and required ~5 ug of analyte to obtain both molecular average and position-specific values in triplicate with precision less than or equal to 1‰.