Position-specific carbon isotope analysis of amino acids by high-resolution gas source IRMS

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Common methods of stable isotope measurement average the isotopic compositions across all non-equivalent sites within a given molecule. Measurement of site-specific isotope distributions can provide additional constraints on molecular origins and histories. Because the number of possible isotopologues for a given molecule increases geometrically with the number of atoms in its molecular structure, various sources of isotopic fractionation potentially create distinctive isotopic fingerprints involving large numbers of independent compositional dimensions.

We are developing a new mass spectrometric technique for measuring the difference in $\delta^{13}C$ between carbon positions in amino acids using a new gas source isotope ratio mass spectrometer, a modified version of the Thermo Scientific DFS™, a reverse-geometry, double focusing, single collector mass spectrometer with nominal mass resolution of 60,000.

Our work initially focuses on alanine because it is the simplest amino acid containing a chiral center. To enhance the volatility of alanine, we converted it to a N-trifluoroacetyl methyl ester derivative, which is a liquid at room temperature. The pure liquid was injected in volumes <1μL into a heated inlet on the DFS. We investigated the relationship between specific peaks in the mass spectrum and the original C sites of the analyte by studying three labelled variants of alanine (obtained from Sigma Aldrich), each of which contain 99 atom % ^{13}C at one of alanine's three carbon sites. We created mixtures of known amounts of labelled and unlabelled alanine, and then measured the $^{13}C/^{12}C$ ratios of various fragment ions (standardized by comparison with unlabelled alanine). These data were used to build a set of transfer functions that describe contributions of each of the three non-equivalent C sites to each of several peaks in the mass spectrum.

To apply this measurement to natural samples with precision of ~1 ‰ or better, we have constructed a heated dual inlet interface suitable for differential measurements of alanine under closely similar instrument conditions, with steady, stable gas flow. This capability will allow a new level of exploration into the isotopic diversity amongst individual carbon atoms in amino acids, with potential applications in astrochemistry and geobiology.