

Isotopic anatomies of organic compounds

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The isotopic ‘anatomies’ of organic molecules (i.e., their proportions of various isotopologues) potentially record temperatures of synthesis, metabolic sources and sinks, photochemical histories, mechanisms and conditions of ‘cracking’ reactions during petroleum genesis, forensic identification, among other things. We describe mass spectrometric methods for measuring a large number and diversity of isotopologues of moderate molecular weight organics (≤ 200 amu), and initial efforts at complementary analysis through microwave spectroscopy.

The measurements we present combine data from the Thermo 253-Ultra (a high resolution multi collector gas source isotope ratio mass spectrometer) and a modified Thermo DFS (a single collector gas source instrument capable of achieving exceptionally high mass resolutions, and modified by us for dual inlet analyses) [1]. We illustrate the capabilities of this system of mass spectrometers using results of three experiments: (1) determination of the multi-isotopologue fractionations associated with evaporation of n-hexane; (2) study of the preservation through EI ionization of site-specific H isotope labels on valproic acid (an anticonvulsant drug); and (3) description of methods for derivatizing amino acids and introducing them to these instruments through heated inlets.

Results to-date indicate that this approach can measure several dozen singly- and multiply-substituted isotopologues, including site-specific differences, for alkanes and organic acids, with accuracy and precision of ~ 0.1 - 0.5 ‰ for ^{13}C and $2\times^{13}\text{C}$ species and ~ 1 - 5 ‰ D and $^{13}\text{C}+\text{D}$ species. Sample sizes are typically 10’s of μmoles . Potential applications of such data will be discussed.

[1] Eiler *et al* (2013), Abstract presented at the Fall AGU.