What are the Limits of Molecular Isotope Analyses ?

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In 1961, Ableson and Hoering pioneered analyses of light stable isotope patterns within and between molecules. This opened exciting vistas into the origins and biogeochemical history of biomarkers and other organic products. But the separation and analysis were laborious and slow. Starting in the 1970s, John Hayes made possible both rapid and precise compound-specific isotope analyses using continuous flow methods. Over the subsequent four decades, his transformative analytical breakthroughs and those he inspired from generations of younger researchers ignited questions across wide-ranging disciplines, including the Earth, climate, medical, ecological, and energy sciences. Recently, the molecular isotopic revolution has advanced once again by novel methods in mass spectrometry and separation science. Here, we will discuss precise analyses of picomolar quantities of whole compounds.

Modifications to a commercial instrument include the high resolving power and low volumetric flow rates of narrow-bore capillary GC, micro-fluidic and narrow-bore components in the combustion interface, and rapid response times and rapid data acquisitions by collector amplifiers and related electronics. The new system, which builds on previous advances [1, 2], is capable of accuracy within ±0.2‰ and standard deviations <0.1‰ for observed 1-10s pmol peaks of pure carbon. For combusted peaks, we can achieve accuracy and precision better than 1‰ for about 100 pmol carbon loaded on the GC column, which translates to about 50 pmol carbon in the ion source. Our pico-CSIA method [3] enables isotopic analysis of biomarkers previously hindered by tiny sample sizes, and broadens the analytical window for molecular isotope applications. We will highlight the history of analytical achievements that made this possible, and explore the theoretical and practical limitations on isotopic analyses of small quantities of carbon. We will also illustrate the picomolar isotope analyses in studies of past carbon cyclig, climates, and life with examples from the Cenozoic and Proterozoic.

[1] Sacks G.L. *et al*. (2007) *Anal. Chem*. 79, 6348-6358.
[2] Tobias H. J. *et al*. (2008) *Anal. Chem*. 80, 8613-8621.
[3] Baczynski *et al*. (2018) *Rapid Comm. Mass Spectrom*., in press; 10.1002/rcm.8084.