

Simultaneous High-Precision Measurement of $^{13}\text{C}/^{12}\text{C}$ and D/H in Short Chain Hydrocarbons using Gas Chromatography-combustion-cavity Ring-down Spectroscopy

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Light stable isotope analysis, and in particular, compound specific isotopic analysis (CSIA), is a valuable tool to elucidate pathways and provide a better insight into geochemical processes. We present here the results of two-element compound-specific isotope analysis of short chain hydrocarbons using the world's first combination of gas chromatography, combustion interface, and a dual cavity ring-down spectroscopy analyzers (GC-C-CRDS) for the simultaneous measurement of $^{13}\text{C}/^{12}\text{C}$ and D/H.

Cavity ring-down spectroscopy (CRDS) is a highly sensitive optical spectroscopy technique, one application of which is to measure the stable isotopic ratios in small molecules. Because it uses a highly reflective optical cavity with many kilometers effective path length, CRDS provides some of the most sensitive and precise optical absorption measurements. Most optical spectroscopy isotopic analysis measures the quantities of each isotopologue independently using their distinct ro-vibrational spectra. The most common isotopes measured with optical spectroscopy are ^{13}C and ^{12}C in carbon dioxide and ^2H , ^1H , ^{18}O and ^{16}O in H_2O . Unlike IRMS, optical spectroscopy can distinguish among isobars, which have nominally identical m/z ratios. The combination of chemical separation, chemical conversion, and CRDS makes a nearly universal tool for isotopic analysis of mixtures. In addition, CRDS can tolerate a variety of compounds mixed with the target. For example, CRDS can measure carbon dioxide and its isotopic $^{13}\text{C}/^{12}\text{C}$ ratio in the presence of oxygen. The CRDS analyzer uses a near infrared laser operating around 6251 cm^{-1} for isotopic CO_2 analysis and around 1392 cm^{-1} for D/H analysis in water.

Using the novel GC-C-CRDS system with dual analyzers, we injected a 75- μl mixture of approximately equal quantities of methane, ethane, and propane into a gas chromatograph using helium as carrier gas. The methane, ethane, and propane were separated in time by 100 to 200 seconds after the chromatograph. Oxygen gas was added, and the hydrocarbons were combusted into CO_2 and H_2O in a catalytic combustor with platinum and nickel, held at 1150°C . The combusted products were combined with dry nitrogen gas to provide sufficient gas flow for the CRDS analyzers and the GC-C effluent of separated and combusted mixture of methane, ethane, and propane was split in two parallel streams flowing into an isotopic CO_2 analyzer for $^{13}\text{C}/^{12}\text{C}$ isotopic ratio analysis on the one hand and into an isotopic H_2O analyzer for D/H isotope ratio analysis, on the other hand. Both measurements were achieved with a precision of 0.95 permil or better. The calibration accuracy was within 3% of the values determined using isotope ratio mass spectrometry (IRMS). Compared with IRMS, the current CRDS-based system is faster in analyzing the compound-specific isotope ratio of both carbon and hydrogen in short chain hydrocarbons, is simpler to operate, and could be made portable for field work.

We anticipate that advances in spectroscopic analysis will improve the precision and accuracy of the CRDS isotopic measurement, making it comparable with IRMS.