



Implementation of a Novel Laser System for Simultaneous Measurement of $^{13}\text{C}/^{12}\text{C}$ and D/H to Food Provenance

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Olive oil samples were analyzed using the world's first simultaneous $\delta^{13}\text{C} + \delta\text{D}$ instrument, the $^{13}\text{C}+\text{D}$ Combustion Module-Cavity Ringdown Spectroscopy (CM-CRDS) Isotope Analyzer. Simultaneous measurements of $\delta^{13}\text{C}$ and δD of the whole oil have been performed on commercially available olive oils produced in Greece, Spain, Italy, California, Lebanon, Israel, Australia and Turkey. Together, the measurements of isotopic ratios of carbon ($^{13}\text{C}/^{12}\text{C}$) and hydrogen (D/H) produce statistically significant differentiation between olive oils from different locations around the globe. Stable isotope ratios are exquisitely sensitive to the biochemistry of plant species and the nutrients available to them in a particular geographical location. Isotope ratios provide detailed knowledge useful for forensic applications through a combination of stable-isotope measurements of carbon ($^{13}\text{C}/^{12}\text{C}$) and hydrogen (D/H) isotopes of organic matter and can help the associations among specific geographic areas through the measurement of these dual isotopes.

We report here on the development of a novel laser spectroscopy based system for the simultaneous analysis of the stable isotope ratios of carbon ($^{13}\text{C}/^{12}\text{C}$) and hydrogen (D/H) that is robust, easy-to-use, and is the first stable isotope ratio analysis system to combine the measurement of $^{13}\text{C}/^{12}\text{C}$ and D/H in one simple analysis from a bulk organic sample.

The system comprises a combustion module to convert the organic sample into CO_2 and H_2O and a Cavity Ring-Down Spectrometer (CRDS) that analyzes the combustion species inside an optical cavity based on the molecular absorption of individual isotopomers. The CRDS uses dual lasers to target the four isotopomers of interest: $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, H_2O and HDO . The system delivers a typical precision of 0.1permil for $\delta^{13}\text{C}$ and 1.5 permil for δD that parallels that achieved by IRMS, but with an unprecedented simplicity that allows scientists to leverage the science and map out the provenance of the analyzed food items.