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# Unique Laser Spectroscopic Approach for High-Precision Compound-Specific Isotope Analysis of 13C/12C and D/H of Combustion Products

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The conventional method to perform high-precision stable carbon isotope measurements with continuous flow-IRMS requires the conversion of the organic sample to carbon dioxide via combustion which is then analyzed to determine the ratio of $^{13}C$ to $^{12}C$. This process also results in the formation of water which can be problematic for measurements using IRMS since the presence of $H_2O$ and $CO_2$ simultaneously in the gas stream can lead to the protonation product $HCO_2^+$ in the mass spectrometer's ion source which interferes with the accurate determination of carbon isotope ratios. To address such a detrimental interference, water is invariably eliminated through the use of permeable membranes or cold traps at the expense of the loss of hydrogen isotopes information embedded in the trapped water molecules. This wasted D/H information is rather valuable due to its large variation in nature and to the additional isotopic dimension it provides for various applications.

Optical spectroscopy-based instruments measure light stable isotope ratios using the shift in the rovibrational absorption peaks generated from the different masses of the isotopomers. The isotopes most commonly measured spectroscopically are $^{12}C$, $^{13}C$ in $CO_2$ and $^{1}H$, $^{2}H$ and $^{16}O$, $^{18}O$ in $H_2O$ molecules. The ability to spectroscopically measure carbon isotopes in $CO_2$ and hydrogen isotopes in $H_2O$ leads to the possibility of measuring carbon and hydrogen isotopes from the combustion products, which is the focus of this work. We present here a unique laser spectroscopic approach for making high-precision compound-specific isotope analysis (CSIA) measurements of both the $^{13}C/^{12}C$ and the $^{2}H/^{1}H$ isotope ratios of the $CO_2$ and $H_2O$ combustion products. The instrument consists of a single front-end comprised of a gas chromatograph (GC) for the separation of the organic mixture coupled to a novel micro-fabricated micro-reactor (MFMR) for combustion of each organic compound into carbon dioxide, water, and other oxidation products, and the precise measurement of the $^{13}C/^{12}C$ in the carbon dioxide gas and $^{1}H/^{2}H$ in the water vapor from the well established infrared spectrum of both gases, using an isotopic $CO_2$ Cavity Ring-Down Spectroscopy (CRDS) analyzer and an isotopic water vapor CRDS analyzer, respectively. Light hydrocarbons are used as our test compounds in this study, owing to their mud-logging diagnostic significance in exploratory and routine oil drilling and their suitability for our present work on a pilot instrumental setup. The analyses of methane, ethane and propane for $^{13}C/^{12}C$ and D/H values achieved a precision level better than 1 permil and 2 permil, respectively. These CRDS results were further compared to the incumbent GC-C-IRMS ($^{13}C/^{12}C$) and GC-Py-IRMS (D/H) techniques and showed excellent agreements in isotopic measurements.