

## Comparison of Carbon and Hydrogen Stable Isotope Analysis by Cavity Ring-down and Isotope Ratio Mass Spectrometry using dual-inlet and gas chromatography of hydrocarbons

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A comparison was made between various stable isotope ratio measurement techniques for the purpose of quantifying each methods capability for use in hydrocarbon analyses applicable to fields such as agriculture, geochemistry, forensics and authenticity testing. Measurement techniques include 1. Cavity Ring-down spectrometry (CRDS) using a Picarro 2120-A with interfaced combustion system to facilitate complete conversion of hydrocarbons to carbon dioxide and water. 2. Isotope Ratio Mass Spectrometry (IRMS) using a Thermo Delta V plus IRMS using off line combustion to carbon dioxide and water with further reduction to hydrogen and dual-inlet measurement 3. Isotope Ratio Mass Spectrometry (IRMS) using a Thermo Delta V plus IRMS interfaced to an Agilent 6890 gas chromatograph for continuous flow separation of component hydrocarbons with combustion to carbon dioxide or reduction to hydrogen using high temperature combustion or pyrolysis respectively. The later two techniques have proven track records for measurement accuracy and precision but require independent analyses of carbon and hydrogen since one needs to oxidize carbon but reduce water to hydrogen prior to measurement. Cavity ring-down spectrometry can however measure the water molecule directly, removing the need for reduction to hydrogen. Using two separate lasers for independent monitoring of carbon dioxide and water frequencies, the isotopic ratios of carbon and hydrogen can be obtained simultaneously. Although the CRDS suffered from memory effects following combustion and transfer of gases early on, new technology has reduced this to acceptable levels for accurate determinations of carbon and hydrogen isotope ratios. Various hydrocarbon materials were used over an extended period of time to determine the best combination of sample size, replicate analyses and combustion column composition and life. The data presented here indicates isotopic ratios of both solid and the more volatile liquid samples compare well with both off-line dual inlet and GC/IRMS methods of analysis.

**Keywords:** Stable isotope analysis, Isotope Ratio Mass Spectrometry, Cavity Ring-down Spectrometry, GC/IRMS.