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Laser-based measurements of δ^{13}C and δ^{2}H methane isotope signatures: precisions competitive with mass spectrometry methods

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In order to understand how and why methane (CH_4) concentrations change over time, it is necessary to understand their sources and sinks. Stable isotope measurements of $^{13}CH_4$:$^{12}CH_4$ and CH_3D:$^{12}CH_4$ ratios constrain the inventory of these sinks and sources. Current measurements often depend on Isotope Ratio Mass Spectrometry (IRMS), which requires extensive sample preparation including cryogenic separation of methane from air and subsequent conversion to either CO_2 or H_2. Here, we detail improvements to a direct-absorption laser spectrometer that enable fast and precise measurements of methane isotope ratios (δ^{13}C and δ^{2}H) of ambient air samples, without such sample preparation.

The measurement system consists of a laser-based direct absorption spectrometer configured with a sample manifold for measurement of discrete samples (as opposed to flow-through measurements). Samples are trapped in the instrument using a rapid sample switching technique that compares each flask sample against a monitor tank sample. This approach reduces instrument drift and results in excellent precision.

Precisions of 0.054 ‰ for δ^{13}C and 1.4 ‰ for δ^{2}H have been achieved (Allan-Werle deviations). These results are obtained in 20 minutes using 4 replicate comparisons to a monitor tank.