

# Real-time analysis of $\delta^{13}\text{C}$ - and $\delta\text{D-CH}_4$ in ambient air with laser spectroscopy: Method development and intercomparison

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In situ and simultaneous measurement of the three most abundant isotopologues of methane using mid-infrared laser absorption spectroscopy is demonstrated. A field-deployable, autonomous platform is realized by coupling a compact quantum cascade laser absorption spectrometer (QCLAS) to a preconcentration unit, called TRace gas EXtractor (TRES). This unit enhances  $\text{CH}_4$  mole fractions by a factor of up to 500 above ambient levels and quantitatively separates interfering trace gases such as  $\text{N}_2\text{O}$  and  $\text{CO}_2$ . The analytical precision of the QCLAS isotope measurement on the preconcentrated (750 ppm, parts-per-million,  $\mu\text{mole/mole}$ ) methane is 0.1‰ and 0.5‰ for  $\delta^{13}\text{C}$ - and  $\delta\text{D-CH}_4$  at 10 min averaging time.

Based on replicate measurements of compressed air during a two-week intercomparison campaign, the repeatability of the TRES-QCLAS was determined to be 0.19‰ and 1.9‰ for  $\delta^{13}\text{C}$  and  $\delta\text{D-CH}_4$ , respectively. In this intercomparison campaign the new in situ technique is compared to isotope-ratio mass-spectrometry (IRMS) based on glass flask and bag sampling and real time  $\text{CH}_4$  isotope analysis by two commercially available laser spectrometers. Both laser-based analyzers were limited to methane mole fraction and  $\delta^{13}\text{C-CH}_4$  analysis, and only one of them, a cavity ring down spectrometer, was capable to deliver meaningful data for the isotopic composition. After correcting for scale offsets, the average difference between TRES-QCLAS data and bag/flask sampling-IRMS values are within the extended WMO compatibility goals of 0.2 and 5‰ for  $\delta^{13}\text{C}$ - and  $\delta\text{D-CH}_4$ , respectively. Thus, the intercomparison also reveals the need for reference air samples with accurately determined isotopic composition of  $\text{CH}_4$  to further improve the interlaboratory compatibility.