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On-site analysis of d13C- and dD-CH4 by laser spectroscopy for the allocation of source processes

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Analysis of the most abundant methane isotopologues 12CH4, 13CH4 and 12CH3D can be used to disentangle source/sink processes (Fischer et al. 2008) and to develop target oriented reduction strategies. Isotopic analysis of CH4 is accomplished by isotope-ratio mass-spectrometry (IRMS) and more recently by mid-infrared laser spectroscopy. For high precision measurements in ambient air, however, both techniques rely on preconcentration of the target gas (Eyer et al. 2014).
We developed a field-deployable analyser for real-time, on-site analysis of CH4 isotopologues which is based on a dual quantum cascade laser absorption spectrometer (QCLAS) in combination with an innovative preconcentration technique named trace gas extractor (TREX). The core part of the 19 ″ rack-mounted preconcentration unit is a highly efficient adsorbent trap attached to the cold end of a Stirling cooler. The system achieves preconcentration factors >500. For fast desorption and optimal heat management, the trap is decoupled from the cooler during desorption. The QCLAS has been developed based on a previously described instrument (Tuzson 2010). It comprises two cw-QC laser sources combined and coupled into an astigmatic multipass absorption cell with 76 m optical path.
The developed technique reaches an unsurpassed precision of 0.1‰ for d13C-CH4 and <0.5‰ for dD-CH4 at 600 s spectral averaging. The potential of the new analytical system for field applications has been shown in June 2014, where the system has achieved an overall repeatability of 0.19‰ for d13C and 1.7‰ for dD-CH4 for repeated target gas measurements. Compatibility of TREX – QCLAS with flask sampling – IRMS for analysis of ambient CH4 fulfilled the extended WMO/GAW compatibility goals of 0.2‰ for d13C-CH4 and 5‰ for dD-CH4.

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