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QCLAS. A compact isotopologue specific analyzer for atmospheric CO_2

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We report on the development of a compact spectrometer based on pulsed quantum cascade (QC) laser. The instrument is specially designed for field applications requiring continuous and high precision CO_2 isotope ratio measurements at ambient air concentration. Long-term, in-situ monitoring is greatly facilitated by the complete cryogenic free operation, which is achieved by employing a quasi room temperature light source and thermoelectrically cooled (TEC) IR-detectors. A dual multipass-cell arrangement allows for simultaneous sample/calibration gas measurements. Spectral analysis is performed on the differential spectrum, leading to a significant improvement of the spectrometer performance due to the cancellation of correlated noise components. A spectral window near 2310 cm^{-1} was selected such that the concentration of all three main stable carbon dioxide isotopologues ($^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{12}C^{16}O^{18}O$) can simultaneously be measured, allowing the determination of both $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios.

Laboratory investigations show that a precision of the isotope ratios well below $0.1^{o}/_{oo}$ is achieved for 200s averaging time. The short-term precision (1σ) for measurements of individual CO_2 isotopologue mixing ratios is at the 0.1 ppmv level.

The instrument performance characteristics were also assessed in a recent field campaign in which we measured vertical profiles of the three CO_2 isotopologues. During a total of two weeks the instrument run continuously and retrieved mixing ratios 100% of the time. First, the spectrometer sequentially analyzed air samples at 1Hz time res-

olution from four intake heights for gradient flux measurements. The derived isotopic ratios were in good agreement with the standard laboratory-based isotope-ratio mass spectrometer measurements made on field-collected flask samples. Repeated measurements (N = 277) of a standard gas cylinder gave a normal distribution with a standard deviation of $0.06^{o}/_{oo}$ and an uncertainty of the mean of $0.01^{o}/_{oo}$. This indicates that a precision significantly better than $0.1^{o}/_{oo}$ can be obtained for long-term measurements with adequate calibration procedure.

Finally, the setup was modified to obtain fast (5Hz) continuous isotope ratio time series for Eddy covariance (EC) flux measurements. Our preliminary results indicate that continuous EC measurements of CO_2 isotopic ratios are feasible. To the best of our knowledge, this is the first field data for such flux measurements.