Performance test, calibration and validation of a novel optical analyzer for continuous and high precision CO_2 isotope ratio measurements

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Introduction

Isotope ratios of carbon dioxide are highly valuable to investigate its sources, sinks and fate at local and global scales. However, such studies generally require extensive and long-term measurements under field conditions, which may not be feasible with standard isotope ratio mass spectrometers (IRMS). Here we present an alternative analytical tool based on direct absorption spectroscopy employing quantum cascade lasers (QCL). The instrument is compact, mobile and inherently has high temporal resolution. It is capable to continuously analyze air samples *in situ*, because it does not require any specific sample preparation.

Instrumental Setup

The instrument was developed for continuous and high precision CO_2 isotope ratio (both $^{13}C/^{12}C$ and $^{18}O/^{16}O$) measurements at ambient air concentration [1,2]. A single-mode, pulsed quantum cascade laser (QCL) operating near 4.3 µm at quasi-room temperature is employed as ligth source. The emitted IR-radiation, is after collimation, divided in two equal beams by a wedged ZnSe beamsplitter and then directed through a dual multi-pass cell assembly. After passing through the cells, the outcoming beams are detected by two TEC photodiodes. A removable Ge-etalon allows for accurate frequency calibration.

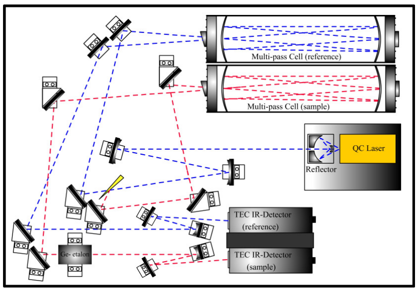

Fig.1 *Schematic diagram of the laser spectrometer optics. The dual-cell arrangement allows for simultaneous sample-reference gas determination which improves the instrument accuracy. Uncertainties in the spectral fitting procedure are considerably reduced by applying the spectral analysis to the ratio of the sample and reference spectra.*

Fig.2 *Picture of the complete instrument. The modular construction results in high mobility and compactness. The use of novel laser and detectors assures cryogen-free operation, thus facilitating long-term measurements.*

Laboratory investigations

- **Precision**: The long-term stability as well as the short term precision of the instruments was evaluated using the Allan variance technique. This indicates an achievable precision in the CO_2 isotope ratios at ambient air concentrations of 0.03 ‰ and 0.05 ‰ for δ¹³C and δ¹⁸O, respectively [2].
- **Accuracy**: The linearity and the accuracy of the δ-scale was determined employing several air tanks which have similar CO_2 mole fractions, but differ in their stable isotope ratio. These gases were previously analyzed by high precision IRMS [3] and then measured by QCLAS. Accuracy of <0.2‰ was achieved for δ¹³C, whereas the δ¹⁸O showed a factor two higher scatter in the correlation plot.

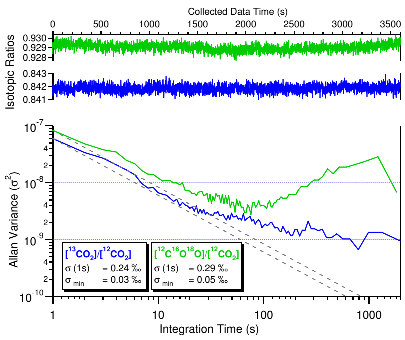

Fig.3 *Time series and associated Allan plots of the simultaneously retrieved spectroscopic ratio of $^{13}CO_2/^{12}CO_2$ and $^{12}C^{16}O^{18}O/^{12}CO_2$, respectively.*

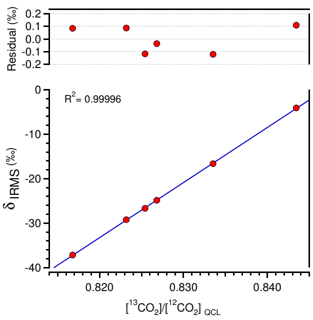

Fig.4 *Comparison of carbon isotope ratios measured by high precision IRMS and QCLAS.*

Calibration & Sampling

Beside the instrumental development, the issue of air sampling and calibration has also been considered. The unit includes gas handling, drying, temperature stabilization and automatic calibration system. No further sample preparation is needed.

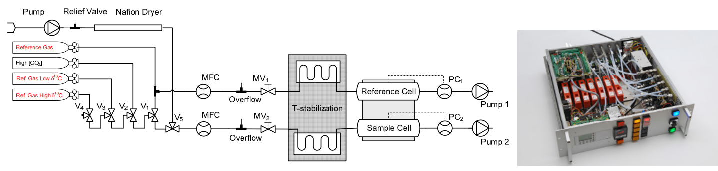

Fig.5 *Schematics and picture of the gas handling unit designed for the QCL spectrometer. The abbreviations are as follows: Vi – 3-way solenoid valve, MV – manual precision valve, MFC – mass flow controller, PC – pressure controller.*

Validation & Field Application

The instrument was successfully operated in various field campaigns, including grass-land ecosystem – atmosphere exchange (gradient and eddy-flux method) and forest soil carbon dynamics studies, and delivered continuous mixing ratio data of the three main CO_2 isotopologues [2,4]. Here we show some relevant results of the field experiments.

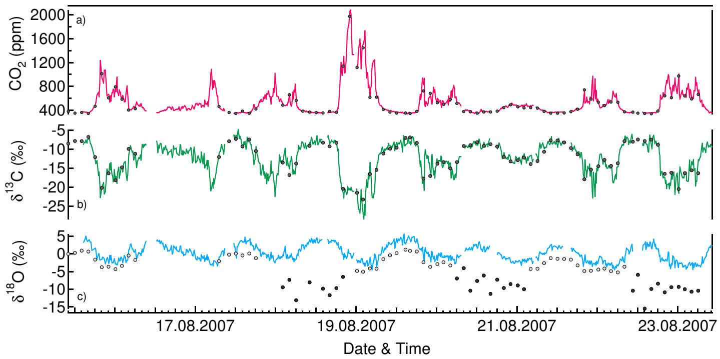

Fig.6 *a) Time series of the CO_2 mixing ratio measured by the QCLAS (line) and with the standardized IRGA (dots). The corresponding δ¹³C and δ¹⁸C values measured by the laser spectrometer are shown in **b)** and **c)**. δ-values measured by IRMS on collected flask samples are also given for comparison. Diurnal variations in the CO_2 concentration indicate ecosystem activity (photosynthesis and respiration). The closed symbols for the δ¹⁸O values indicate sampling issues with small volume metal flasks and possible isotope exchange effects between water and carbon dioxide.*

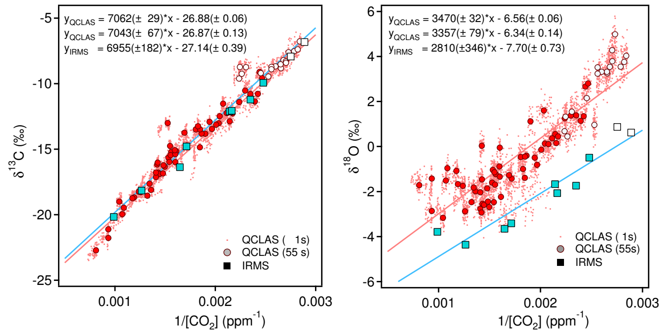

Fig.7 *Keeling plots for data collected during 24 hours at measurement height of 0.1 m. Isotope ratios are plotted against the inverse of CO_2 concentration. The intercept and the slope of the linear regression is given together with their standard deviation. Besides the QCLAS data points (circles), the field-collected flask samples are also plotted (rectangles). The open symbols represent the day-time, while the closed symbols the night-time measurements. The high temporal resolution (one second) QCLAS data are also presented in the background (dots).*

Conclusion & Outlook

This poster illustrates the development of a QCL based spectroscopic technique for the simultaneous and high precision measurement of $^{12}CO_2$, $^{13}CO_2$ and $^{12}C^{16}O^{18}O$ in atmospheric carbon dioxide. Long-term and continuous measurements are made possible by employing cryogen-free components for both the laser and detector. Furthermore, an adequate gas handling and calibration unit has been developed, which assures a rigorous control of gas temperatures, pressures and flow rates. At the moment the instrument is used for a feasibility study on a high alpine site (Jungfraujoch, Switzerland, 3580 masl).

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