Name of research institute or organization:

Empa, Swiss Federal Laboratories for Materials Science and Technology

Title of project:

Continuous measurement of stable CO_2 isotopes at Jungfraujoch, Switzerland

Part of this programme:

ICOS

Project leader and team:

Dr. Lukas Emmenegger, project leader
Dr. Béla Tuzson

Project description:

Isotopic composition measurements of atmospheric CO_2 deliver valuable information about the involved source- and sink processes and their dynamics at local, regional and continental scales. The continuous, in situ, and real-time isotope analysis at the Jungfraujoch based on quantum cascade laser absorption spectrometer (QCLAS) is a world-wide unique opportunity to gain unprecedented insight into the characteristics of atmospheric CO_2.

The three main CO_2 isotopologue mixing ratios ($^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{12}C^{18}O^{16}O$) have simultaneously been recorded since December 2008, providing the first long-term, continuous time series of its kind at a remote location. The spectroscopic data and numerous instrumental parameters are acquired at 1 Hz time resolution. In 2015, the calibration routines and the data processing procedures of the QCLAS have been improved and optimized for systematic reporting of hourly calibrated data. This assures compatibility with international procedures and guarantees long-term traceability to the WMO and VPDB scales (Max Planck Institute for Biogeochemistry, MPI-BGC) for the CO_2 concentration and the stable isotope ratios $\delta^{13}C$ and $\delta^{18}O$. Current calibration is based on four secondary standards and three working standards. Possible instrumental drifts are determined at 15 minutes time intervals using a pressurized air cylinder. Furthermore, the cooling system for the laser and detector has been upgraded to obtain a thermal control of ± 0.05°C. Thus, the laser temperature can be kept at a constant value within ± 1 mK over extended periods of time, i.e. days or weeks. To achieve this, it was crucial to shield the optical module against temperature variations in the Sphinx Laboratory through a combination of active and passive elements, leading to a dampening factor > 50 in the optical system. The analytical precision under normal operating conditions was reassessed and found to be <0.03 ‰ for both $\delta^{13}C$ and $\delta^{18}O$ for an averaging time of 10 minutes.

In addition, the QCLAS participated in the WMO/IAEA Round Robin 6 Comparison Experiment (http://www.esrl.noaa.gov/gmd/ccgg/wmorr/wmorr_results.php) to assess the instrument capability to hold the link to the WMO recommended level under field operation. Table 1 shows the summary of the results for the CO_2 isotope measurements. The last row indicates the absolute deviation of the QCLAS values from the VPDB scale. Within the reported uncertainty, the values for both isotope ratios are approaching the WMO recommended level of network compatibility (0.01 ‰ and 0.05 ‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively) regardless of the CO_2 concentration. It appears that there is a systematic offset of -0.07 ‰ and -0.155 ‰ for $\delta^{13}C$ and $\delta^{18}O$ in the reported QCLAS values. As the precision of the QCLAS is better than these offset values, it is possible that the systematic error originates from the calibration gases. The larger uncertainty range reported for the $\delta^{18}O$ values is due to the difficulty of interpolating the δ - scale from -7.6 ‰ (highest value from calibration gases) towards -1 ‰, value typical for ambient air CO_2.

Table 1: Summary of the WMO/IAEA Round Robin 6 comparison experiment as reported by NOAA. The stable isotopes of CO_2 values have been assigned by the Institute of Arctic and Alpine Research (INSTAAR), Stable Isotope Laboratory (SIL), University of Colorado, USA. Two gas cylinders with high (H) and low (L) CO_2 mole fractions were analyzed and the difference against the reference lab (INSTAAR) calculated. The MPI-BGC results are included, because the QCLAS reference scale is linked to this lab.

Lab – Ref	$\Delta\delta^{13}C$ (‰)		$\Delta\delta^{18}O$ (‰)	
	H	L	H	L
INSTAAR (IRMS)	0.000 ± 0.011	0.000 ± 0.011	0.000 ± 0.040	0.000 ± 0.029
MPI-BGC (IRMS)	-0.048 ± 0.024	-0.043 ± 0.028	-0.056 ± 0.046	-0.031 ± 0.053
Empa (QCLAS)	-0.120 ± 0.041	-0.116 ± 0.041	-0.205 ± 0.175	-0.194 ± 0.153
Empa – MPI	-0.072 ± 0.047	-0.073 ± 0.049	-0.149 ± 0.181	-0.163 ± 0.162

Key words:

Isotope ratio measurements, carbon dioxide, laser spectroscopy, quantum cascade laser

Collaborating partners/networks:

ICOS – Integrated Carbon Observation System
Max Planck Institute for Biogeochemistry, Jena, Germany
University of Berne, Switzerland
Alpes Lasers SA, Switzerland

Scientific publications and public outreach 2015:

Conference papers

Emmenegger, L., MIR Spectroscopy for environmental applications, Swiss Photonics Workshop, Dübendorf, Switzerland, January 15, 2015.

Emmenegger, L., B. Tuzson, J. Jágerská, H. Looser, M. Mangold, and J. Mohn, MIR Spectroscopy beyond trace levels - environmental and industrial applications, CLEO, San Jose, USA, May 10-15, 2015.

Steinbacher, M., B. Tuzson, Y. Poltera, G. Martucci, A. Haefele, F. Conen, M. Leuenberger, and L. Emmenegger, Swiss Contribution to Atmospheric Observations in ICOS (Integrated Carbon Observation System), Swiss Global Change Day, Bern, Switzerland, April 1, 2015.

Magazine and Newspapers articles

https://www.axetris.com/de-ch/axetris-news/1509_axag_mfd-ss-top-of-europe-climate-change-research/

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