SI Traceable Isotope Ratios of Carbon Dioxide

– a Feasibility Study

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– Advancing Optical Isotope Ratio Spectroscopy

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Characterisation of optical isotope analysers for carbon dioxide in the framework of the EMPIR project SIRS

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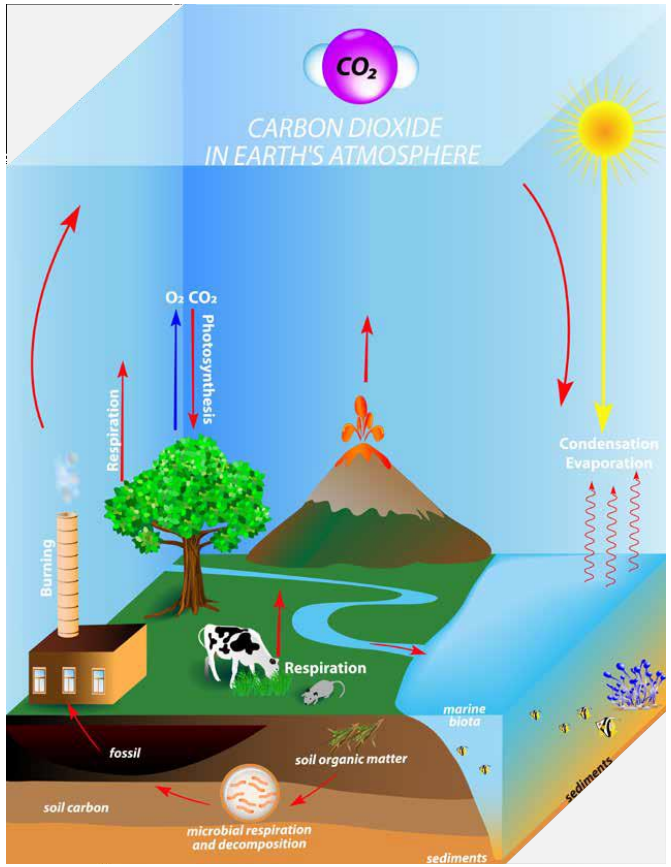
Introduction



EMPIR review conference, SIRS poster, by P. Brewer

Isotopic composition of carbon dioxide $\delta^{13}C$ and $\delta^{18}O$ can be used to discriminate between natural and various manmade sources of CO_2 [1]. Within the EMPIR project “Metrology for Stable Isotope Reference Standards” (SIRS) [2,3] advanced spectroscopic methods are applied.

[1]GAW report, 242. 19th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2017) (27-31 August 2017; Dübendorf, Switzerland)

[2] https://www.vtt.fi/sites/SIRS

[3] https://www.euramet.org/research-innovation/research-empir

Introduction

$$\delta^{13}\mathrm{C} = \frac{^{13}r}{^{13}r_{ref}} - 1 = \frac{^{13}\mathrm{R}}{^{13}r_{ref}} - 1$$

Isotope ratio and "delta" value

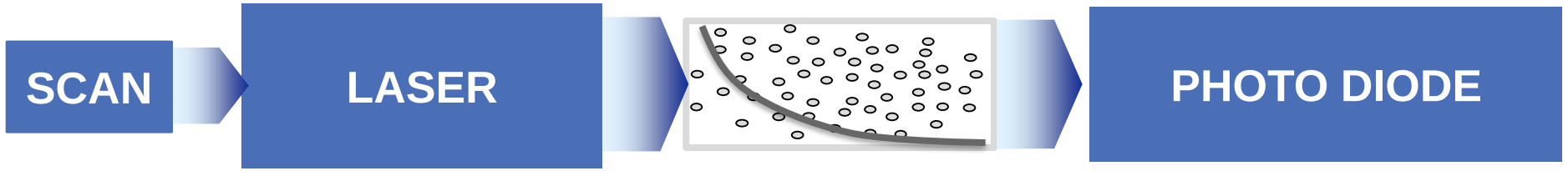
$$^{13}\mathrm{R} = \frac{x(^{13}\mathrm{C}^{16}\mathrm{O}_2)}{x(^{12}\mathrm{C}^{16}\mathrm{O}_2)}$$

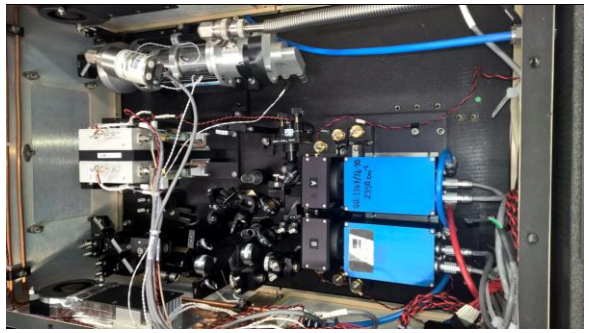
Isotopologue ratio

$$x\,(^{13}\mathrm{C}^{16}\mathrm{O}_2) = \frac{A(^{13}\mathrm{C}^{16}\mathrm{O}_2)}{S_T(^{13}\mathrm{C}^{16}\mathrm{O}_2)} \times \frac{k_B \cdot T}{L \cdot p}$$

Spectroscopic measurement of isotopologue amount fraction
A – absorption line area,
S_T – line strength, p – gas pressure, T – gas temperature,
L – optical path length

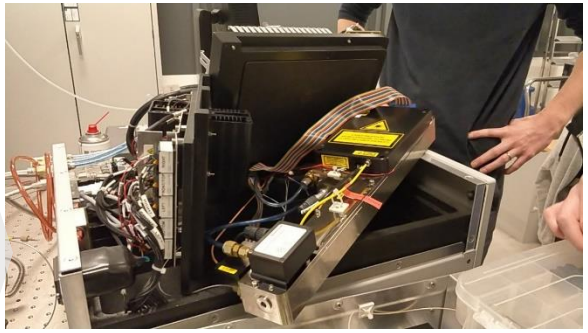
Optical isotope analysers





Optical isotope ratio spectrometer at RUG

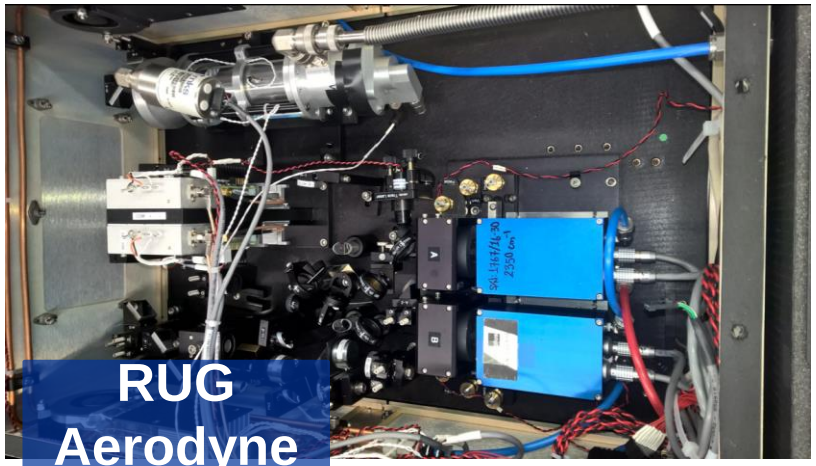
Optical isotope ratio spectrometer at PTB



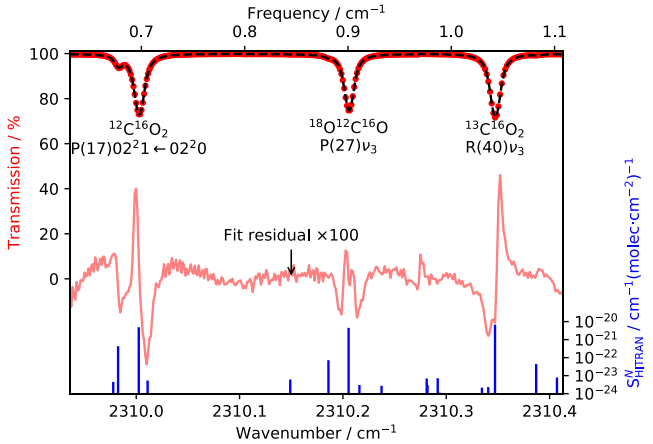
	OIRS at RUG [4]	OIRS at PTB [5]
Light source	ICL	DFG PPLN
Center wavelength	4.3 µm	4.3 µm
Gas cell pathlength	36 m	5.4 m
Gas cell pressure	50 hPa	100 hPa
Gas cell temperature	294 K	311 K

[4] Aerodyne TILDAS, e.g. J. B. McManus, D. D. Nelson, and M. S. Zahniser, Opt. Exp., **23**, 6569 (2015)
[5] Thermo Delta Ray, e.g. J. Braden-Behrens, Y. Yan, A. Knohl, Atoms. Meas. Tech., **10**, 4537–4560 (2017)

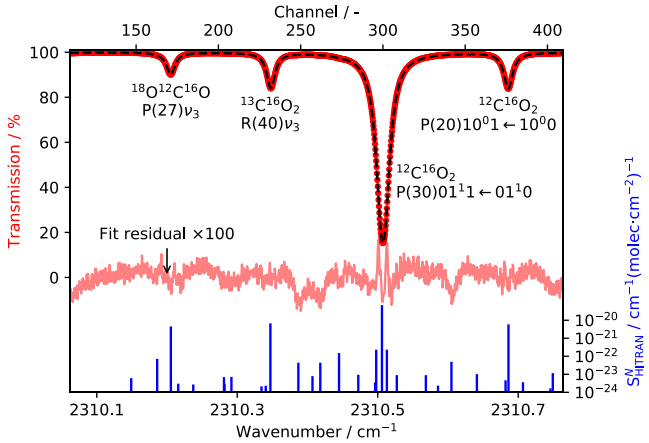
Measured spectra



RUG
Aerodyne
TILDAS

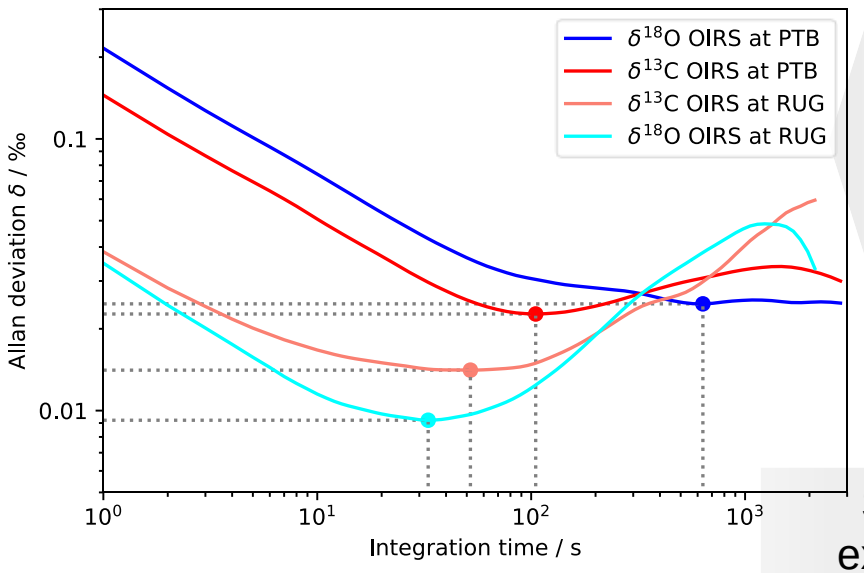


PTB
Thermo Scientific
Delta Ray



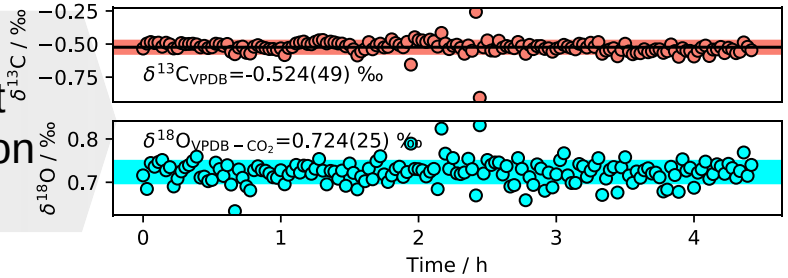
Presented at EGU General Assembly 2019, April 7-12, 2019, Vienna, Austria and The 20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2019), September 2-5, 2019, Jeju, Korea.

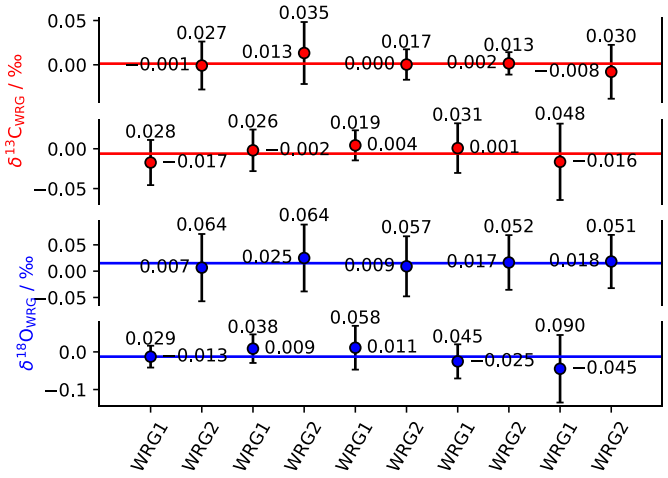
Instrument stability



Instruments at PTB and RUG: white noise dominates up to ~100 seconds, significant drifts are on the timescale of 200-500 seconds

Single tank experiment at RUG: integration 35 sec





Reproducibility test at PTB:
24 h measurements,
2 h each WRG,
5 min integration time

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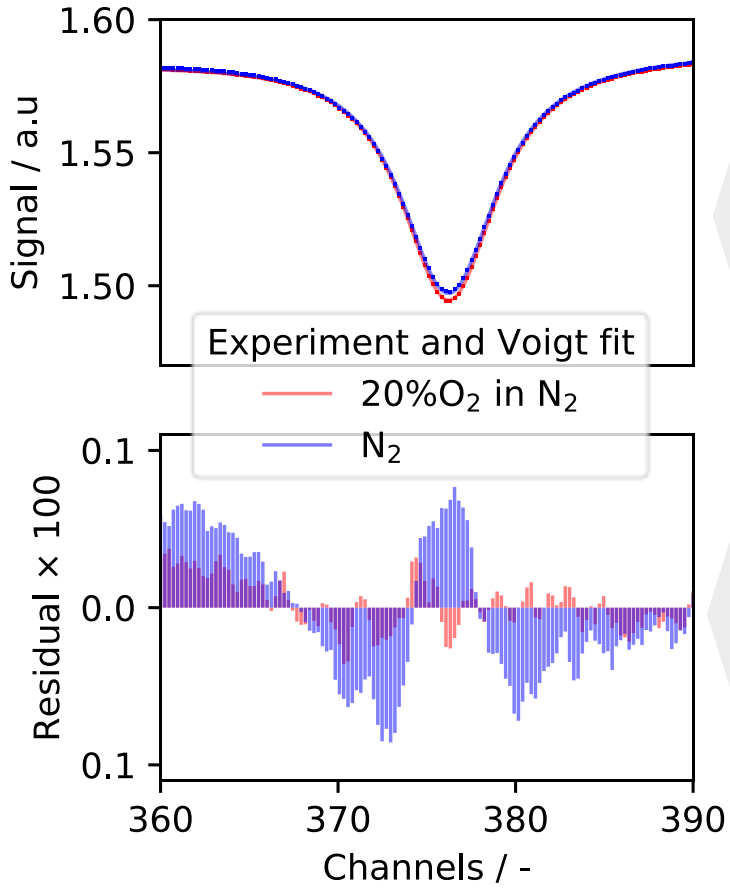
Study of matrix effects

$$w_L = \sum_{i}^{matrix} p x_i \gamma_i(m, v, T)$$



$^{12}C^{16}O_2$ transition P(20) in 1001-1000 band
p = 100 hPa, T = 311 K,
$x CO_2$ = 450 ppm

Fit residuals:
Voigt fit with fixed p-broadening coefficient for 20% O_2 in N_2

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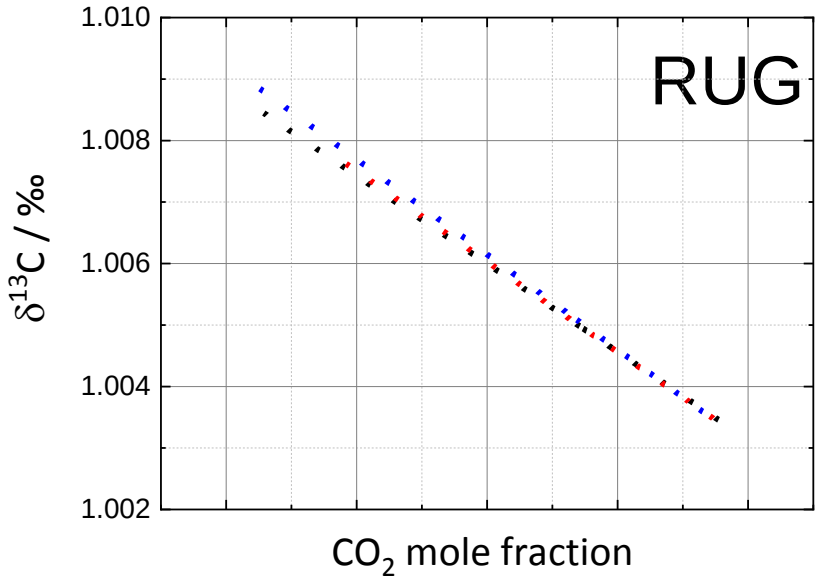
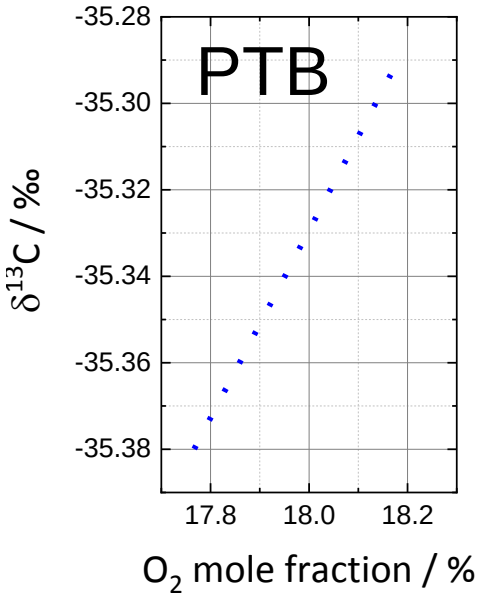
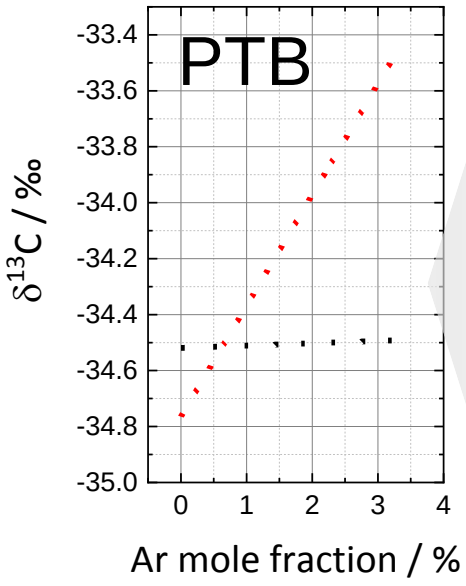
Study of matrix effects







Partial elimination of matrix effect by setting w_L as free fitting parameter

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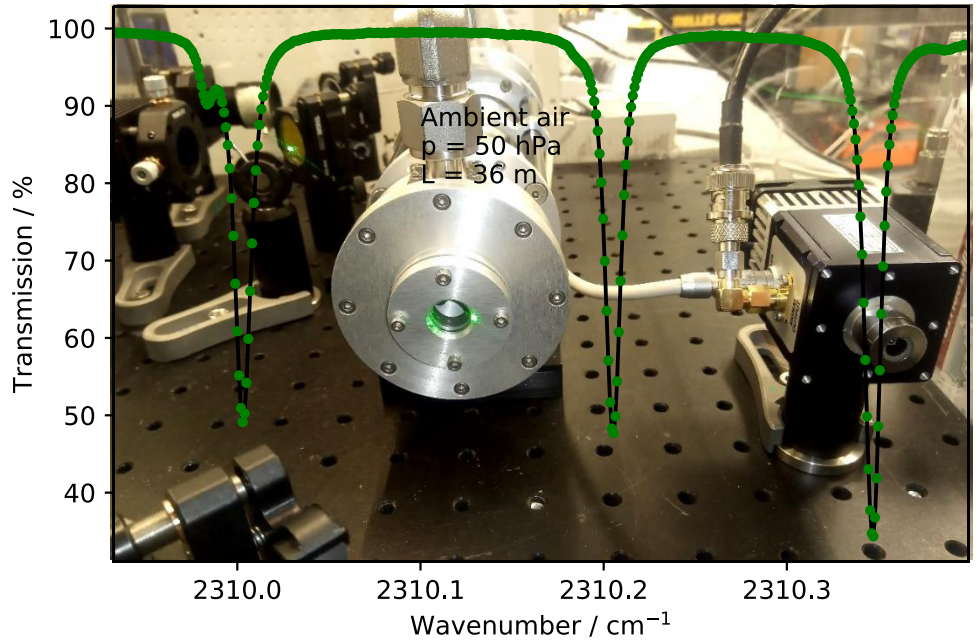
OIRS in VTT



CO_2 optical isotope ratio spectrometer under construction in VTT. It deploys a 4.3 µm ICL and Aerodyne multi-pass cell with 36 m path length [6].

[6] J. McManus, P. Kebabian, and M. Zahniser, Appl. Opt., **34**, 3336–3348 (1995).

- Two-stage thermal control system will be used to reach the target uncertainties of 0.1 ‰ for $\delta^{13}C$-CO_2 and 0.5 ‰ for $\delta^{18}O$-CO_2.

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FTIR in INRIM

- FTIR calibration based on synthetic spectra, generated by means of a radiative transfer calculation code MALT. B-FOS, a software developed at the BIPM allowed to interface MALT and the FTIR management software.
- The uncertainty obtained for $\delta^{13}C\text{-}CO_2$ measurements is around 0.1 ‰, at a nominal CO_2 mole fraction of 400 µmol mol^{-1} in air.

Presented at EGU General Assembly 2019, April 7-12, 2019, Vienna, Austria and The 20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2019), September 2-5, 2019, Jeju, Korea.

Conclusion

Results:

- Two commercial optical isotope ratio spectrometers for $\delta^{13}C$ and $\delta^{18}O$ measurements of CO_2 at ambient air concentrations have been characterized at PTB and RUG, normalized precision 1.35 and 5.4 ‰ m $Hz^{1/2}$, respectively.
- Extensive studies of matrix gas effects and CO_2 concentration have been conducted. Observed dependence of δ-values on matrice can be partially eliminated by improved spectral fit.
- An OIRS is being developed in VTT.
- INRIM developed FTIR method for $\delta^{13}C$.

Plans:

- Comparison of OIRS measurement results between partners.
- Comparison of OIRS and IRMS for several reference materials.