This presentation originally intended to be a poster has suffered from Corona-related restrictions, both

- *at the preparation phase, and*
- *for the presentation.*

The authors wish to thank all partners and EGU2020 participants for their understanding

Physikalisch-Technische Bundesanstalt
Braunschweig and Berlin
National Metrology Institute

Metrology for calibration strategies and uncertainty assessments for spectroscopic MID-IR CO_2 isotope ratio measurements

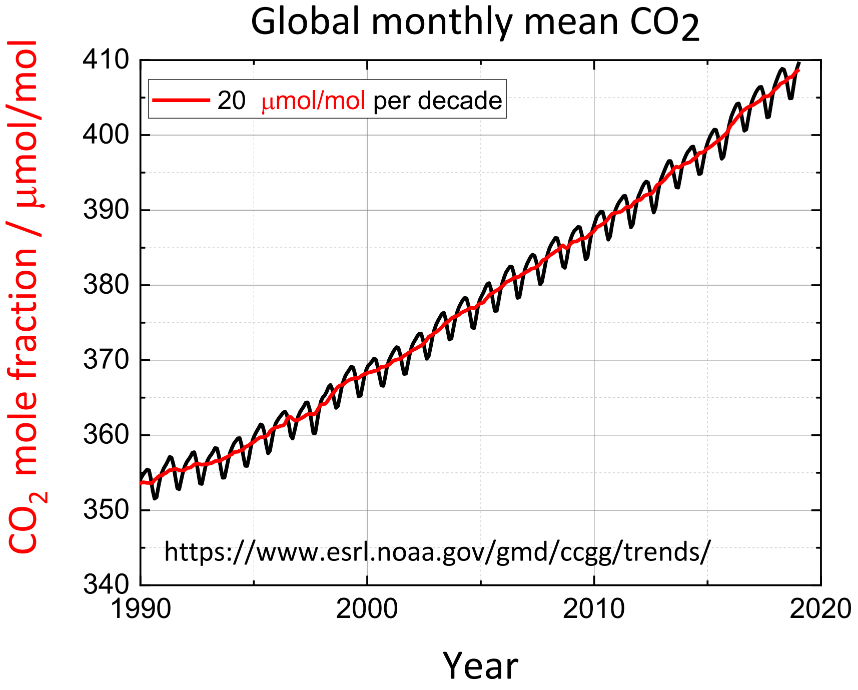
EGU GA 2020, web presentation – originally intended to be presented as poster on board X5.275, May 5th.

Ivan Prokhorov, Ian Chubchenko,
■ Olav Werhahn, and Volker Ebert

The author list is updated to read as following:

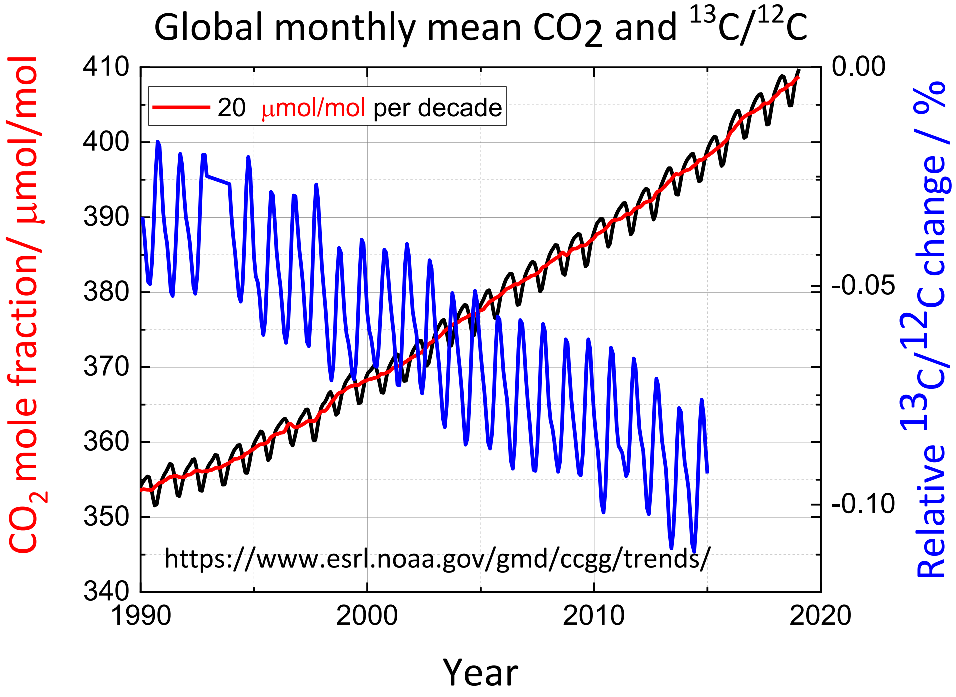
- Ivan Prokhorov is now with the Laboratory for Air Pollution / Environmental Technology, Empa, CH-8600 Dübendorf, Switzerland
- Ian Chubchenko is with the D.I.Mendeleyev Institute for Metrology (VNIIM), 19 Moskovsky pr., St. Petersburg, 190005 Russia, and ITMO University, 49 Kronverksky Pr., St. Petersburg, 197101, Russia
- Olav Werhahn, and Volker Ebert are with the PTB / cf. last page

CO_2 is an important greenhouse gas



How to discriminate man-made from natural contribution in the atmosphere?

CO_2 is an important greenhouse gas



How to discriminate man-made from natural contribution in the atmosphere?

About 1.1% of CO_2 contains ^{13}C isotope

Plants "prefer" ^{12}C over ^{13}C

Fossil fuel is depleted in ^{13}C

Combustion produces CO_2 with less ^{13}C

Isotopes are the key to understand sinks and sources of CO_2

Isotopic composition of CO_2

Isotopes - nuclides having the same atomic number but different mass numbers.

natural abundance:

^{12}C (98.9%)	^{13}C (1.1%)	$^{14}C_{(radioactive)}$
^{16}O (99.8%)	^{18}O (0. 2%)	^{17}O (0.04%)

delta-value (sub-‰ variations):

$$\delta^{13}\mathrm{C} = \frac{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{sample}}}{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{reference}}} - 1$$

IAEA
International Atomic Energy Agency

IAEA reference materials:
NBS 18 *(exhausted)*
IAEA 603 *(replacement)*

solids

Isotopic composition of CO_2

Isotopes - nuclides having the same atomic number but different mass numbers.

Isotopologues a molecular entity that differs only in isotopic composition

- ➢ *Same pathway in chemical reactions*
- ➢ *Slightly different physical properties*

Isotopologue i				
No	Symbol	Mass (u)[a]	Rel. abundance $n_i/\Sigma_j n_j$ (mol/mol)	Rel. contribution to mass (%)
1	$^{12}C^{16}O_2$	44	$9.842 \cdot 10^{-1}$	100.000
2	$^{13}C^{16}O_2$	45	$1.100 \cdot 10^{-2}$	93.636
3	$^{12}C^{16}O^{18}O$	46	$3.947 \cdot 10^{-3}$	99.785
4	$^{12}C^{16}O^{17}O$	45	$7.478 \cdot 10^{-4}$	6.364
5	$^{13}C^{16}O^{18}O$	47	$4.413 \cdot 10^{-5}$	96.710
6	$^{13}C^{16}O^{17}O$	46	$8.361 \cdot 10^{-6}$	0.211
7	$^{12}C^{18}O_2$	48	$3.957 \cdot 10^{-6}$	99.578
8	$^{12}C^{17}O^{18}O$	47	$1.500 \cdot 10^{-6}$	3.286
9	$^{12}C^{17}O_2$	46	$1.421 \cdot 10^{-7}$	0.004
10	$^{13}C^{18}O_2$	49	$4.424 \cdot 10^{-8}$	100.000
11	$^{13}C^{17}O^{18}O$	48	$1.676 \cdot 10^{-8}$	0.422
12	$^{13}C^{17}O_2$	47	$1.588 \cdot 10^{-9}$	0.003

Table taken from Prokhorov, I., Kluge, T. & Janssen, C. Optical clumped isotope thermometry of carbon dioxide. Sci Rep 9, 4765 (2019).

Absorption spectrum of CO_2 isotopologues

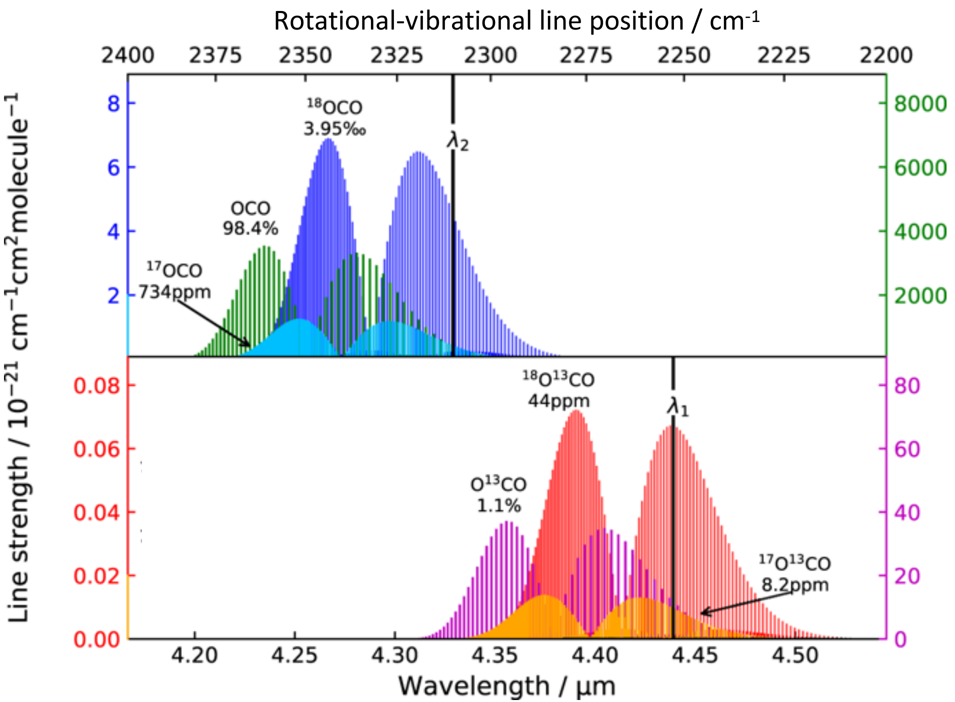
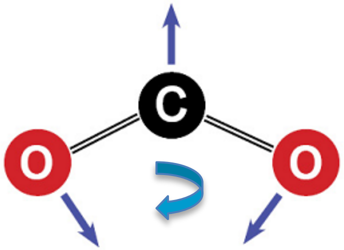


Figure adapted from Prokhorov, I., Kluge, T. & Janssen, C. Optical clumped isotope thermometry of carbon dioxide. Sci Rep 9, 4765 (2019).



ro-vibrational motion

Boltzmann constant

$$x(^{13}\mathrm{C}^{16}\mathrm{O}_2) = A\,\frac{k_\mathrm{B}\cdot T}{S\cdot p\cdot L}$$

temperature

optical path length

pressure

absorption line area

line strength of respective molecular transition

Main goals of SIRS

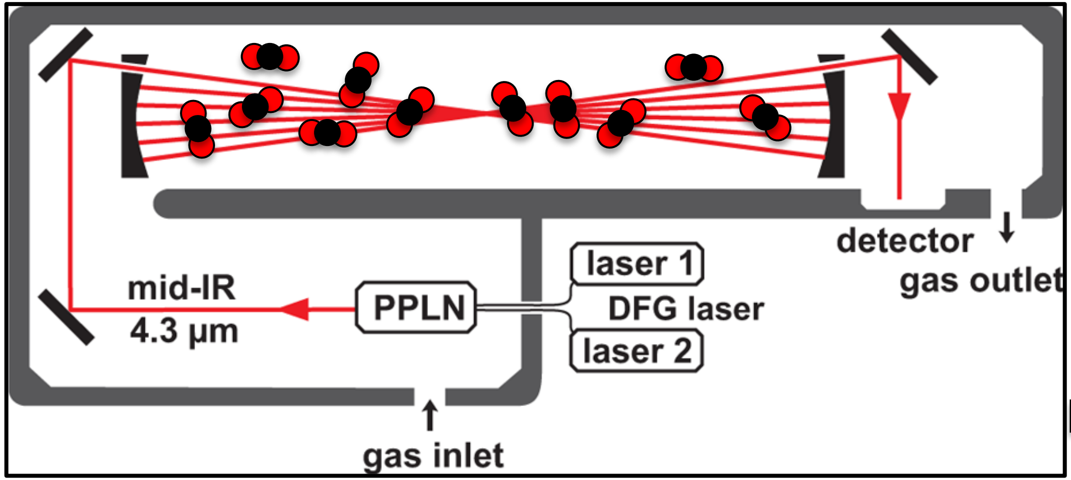
„Metrology for Stable Isotope Reference Standards"
(2 M€, 3 years research project within EMPIR, HORIZON2020)

WP1:
- Static and dynamic pure CO_2 and air-CO_2 isotope reference materials
- Remeasure isotope ratios in international standards to provide data for SI traceability

WP3:
- **Advance spectroscopic CO_2 isotope ratio measurements**
- **Spectral line data measurements**

Optical isotope ratio measurements

Tunable Diode Laser Absorption Spectroscopy

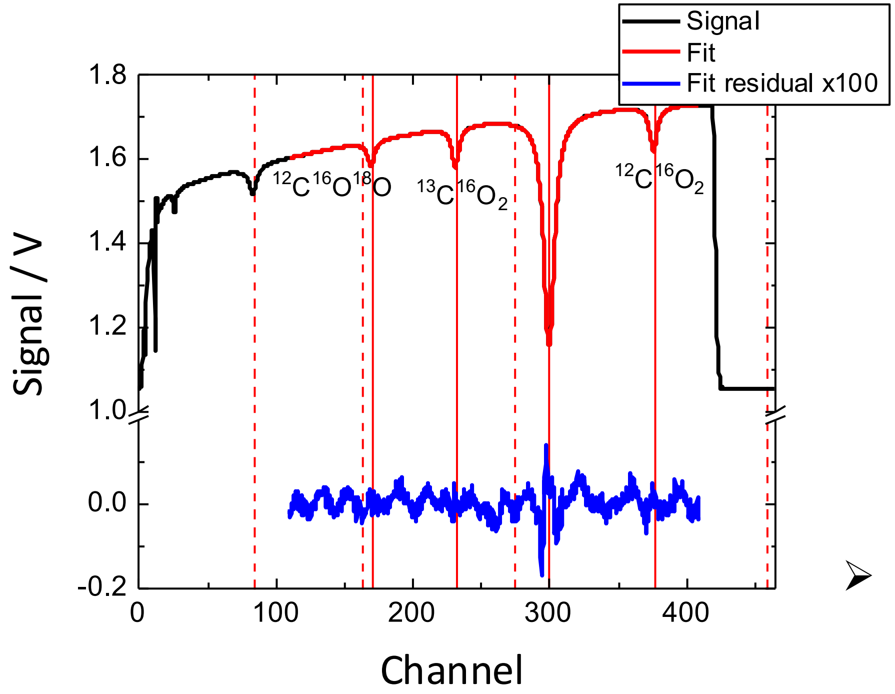


Thermo Scientific Delta Ray

- absorption inside the gas cell (CO_2 in air)
- p = 100 mbar, T = 310 K, L = 5.4 m

portable optical
isotope ratio spectrometer

Optical isotope ratio measurements



$$x(^{13}\mathrm{C}^{16}\mathrm{O}_2) = A\,\frac{k_\mathrm{B}\cdot T}{S\cdot p\cdot L}$$

$$^{13}\mathrm{C}/^{12}\mathrm{C} = \frac{A(^{13}\mathrm{C}^{16}\mathrm{O}_2)}{A(^{12}\mathrm{C}^{16}\mathrm{O}_2)}\,\frac{S(^{12}\mathrm{C}^{16}\mathrm{O}_2)}{S(^{13}\mathrm{C}^{16}\mathrm{O}_2)}$$

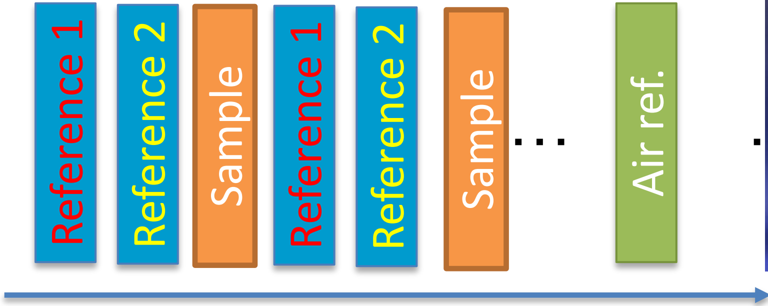
$$\boxed{u(S)>1\% \quad\rightarrow\quad u(S)<0.1\%}$$

- More accurate line data is required (in progress @ PTB)
- Towards *"Optical Transfer Standard"*

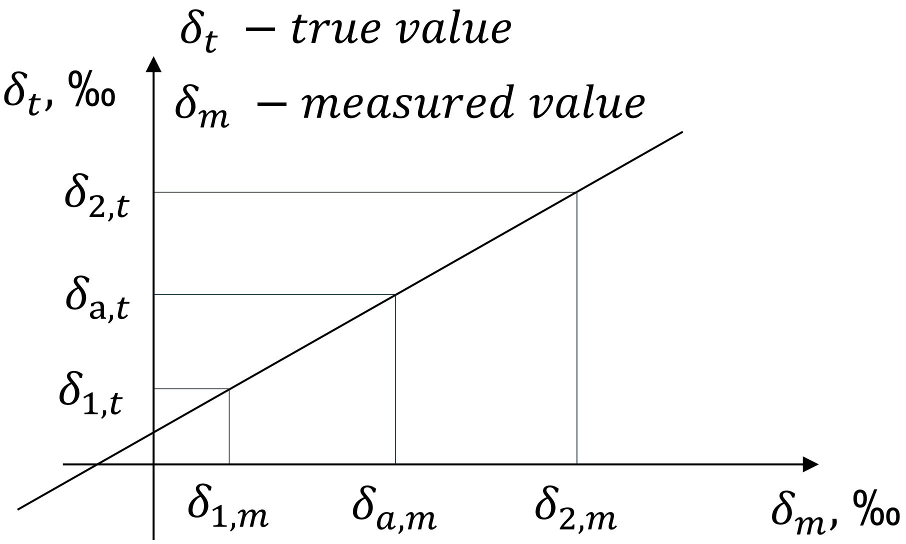
Calibration based on reference gases

$$\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{reference}} = \left(\frac{A(^{13}C^{16}O_2)}{A(^{12}C^{16}O_2)}\right)_{sample} \Big/ \left(\frac{A(^{13}C^{16}O_2)}{A(^{12}C^{16}O_2)}\right)_{reference}$$

$$\delta\,^{13}C = \frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{reference}} - 1$$



Measurement sequence (loop)



$$\delta_{2,t} = \delta_{2,m} + \frac{2}{3}\left(\delta'_{2,m} - \delta_{2,m}\right)$$

$$\delta_{1,t} = \delta_{1,m} + \frac{1}{3}\left(\delta'_{1,m} - \delta_{1,m}\right)$$

$$\delta_{a,t} = \frac{\delta_{1,t} - \delta_{2,t}}{\delta_{1,m} - \delta_{2,m}}\left(\delta_{a,m} - \delta_{1,m}\right) + \delta_{1,t}$$

Photography not allowed

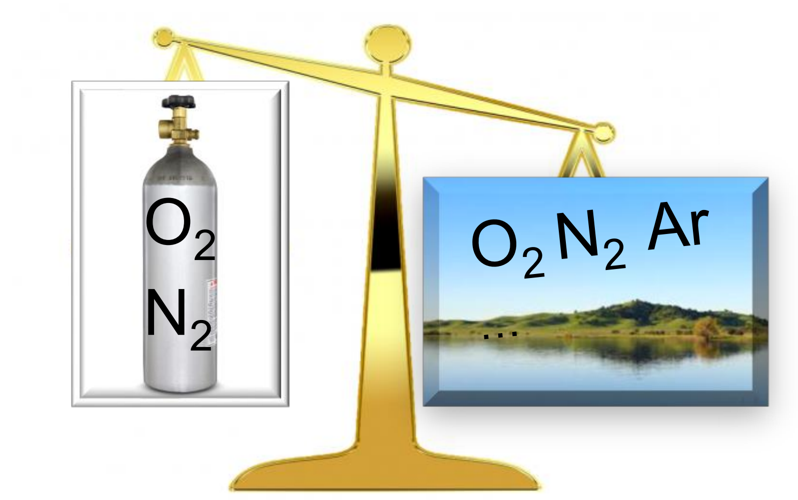
Please pay attention

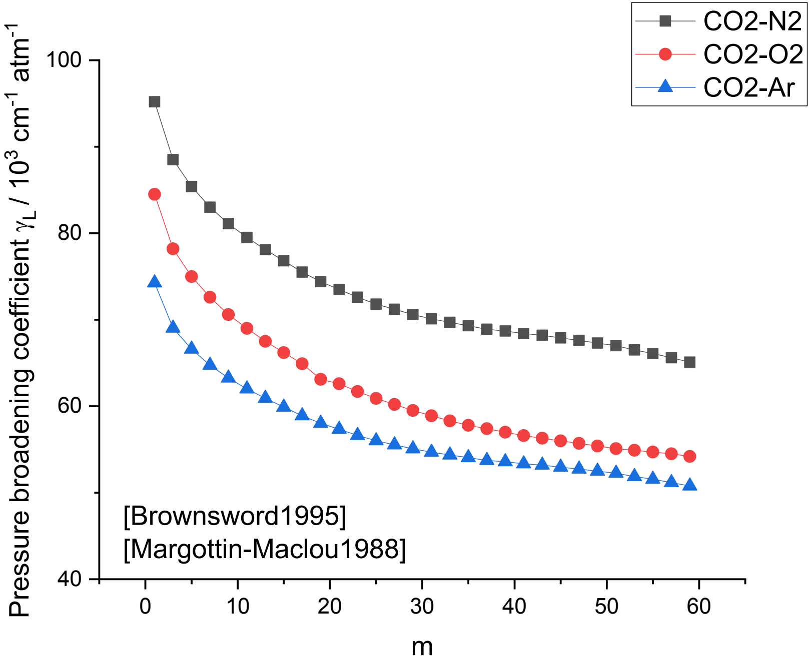
unpublished data

Thanks in advance !

Prokhorov, I., I. Chubchenko, G. Li, O. Werhahn, and V. Ebert, "Eliminating the effect of air composition in optical isotope ratio spectrometer", in preparation.

Lab to field / case study on air matrix





- No standard for "<u>synthetic</u>" air composition in place
- Mismatch in air matrices between reference and sample leads to artificial bias in δ values

Pressure broadening coefficient γ_L is a *<u>fixed</u>* parameter in default fitting model approach (!)

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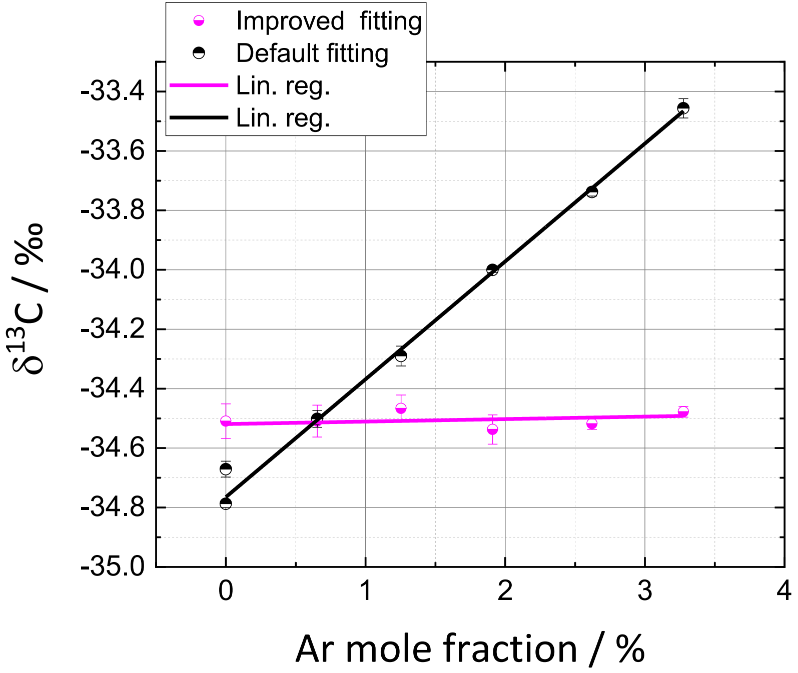
Lab to field / case study on air matrix



Matrix mismatch = broadening parameters are not appropriately adapted to the experimental situation

	Ar (‰/%)	O_2 (‰/%)
$\delta^{13}C$	0.39	-0.14
$\delta^{18}O$	-0.32	0.22

A slighly modified fitting model approaches the matrix mismatch problem ***– and solves it!***

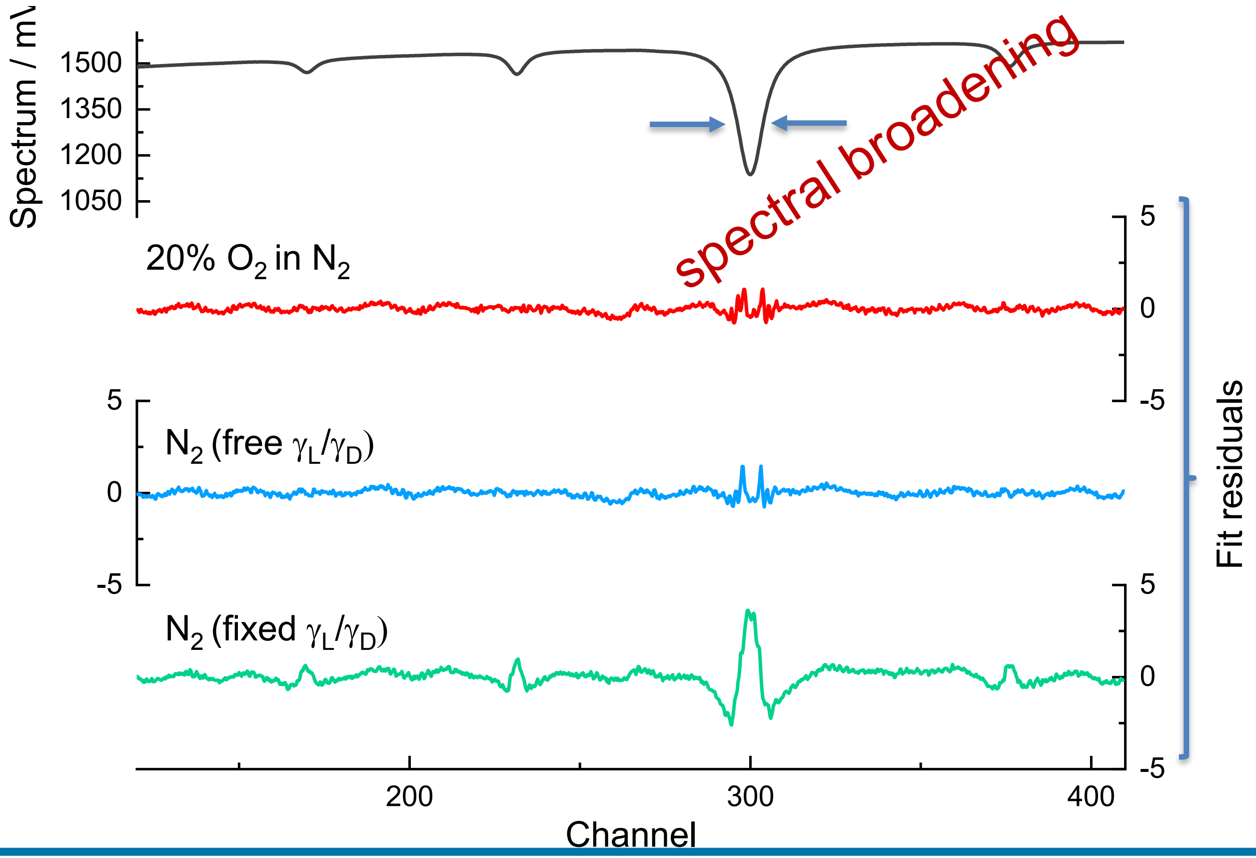
Prokhorov, I., I. Chubchenko, O. Werhahn, G. Li, and V. Ebert "Eliminating the effect of air composition in optical isotope ratio spectrometer", in preparation.

Lab to field / case study on air matrix

$\delta^{13}C$	-4.33(4) ‰
$\delta^{18}O$	-17.47(7) ‰

$\delta^{13}C$	-4.37(8) ‰
$\delta^{18}O$	-17.46(5) ‰

$\delta^{13}C$	-7.94(1) ‰
$\delta^{18}O$	-14.69(3) ‰



Prokhorov, I., I. Chubchenko, O. Werhahn, G. Li, and V. Ebert "Eliminating the effect of air composition in optical isotope ratio spectrometer", in preparation.

Uncertainty budget

		Default (Factory)		Drift correction + Linearity calibration (400-800 ppm) + improved PTB-fit approach	
		δ13C / ‰	δ18O / ‰	δ13C / ‰	δ18O / ‰
	Reproducibility, u_{repr}	0.02	0.03	0.02	0.03
	Calibration, u_{cal}	0.06	0.1	0.06	0.1
	Concentration dependence, u_{conc}	0.01	0.01	0.001	0.001
	Matrix mismatch effect, u_{matrix}	0.08	0.07	0.001	0.001
Combined standard uncertainty, u		0.10	0.13	0.06	0.10
Expanded uncertainty, U *(k=2, 95% confidence interval)*		0.20	0.25	0.13	0.21

$$U = 2\sqrt{u_{repr}^2 + u_{cal}^2 + u_{conc}^2 + u_{matrix}^2}$$

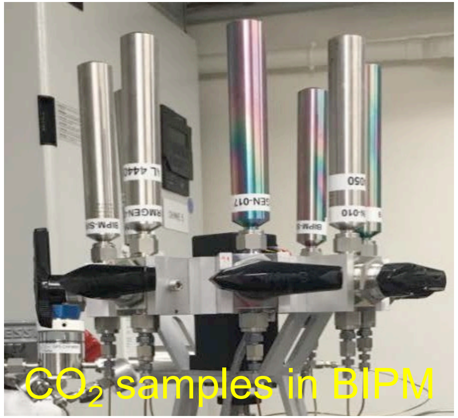
Outlook

- Characterization of a *gold standard* candidate, commercial Optical Isotope Ratio Spectrometer (OIRS) is completed at PTB (PTB in early 2019)

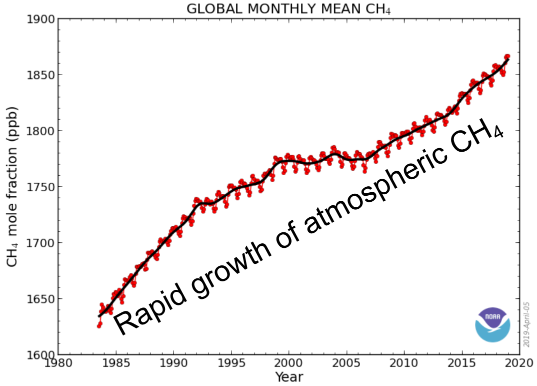
- Comparison of optical isotope ratio methods within SIRS is ongoing (to be finished in summer 2020)

- CCQM-P204 *pilot study* on $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotope ratios in *pure* CO_2 taking place in 2020
  - CCQM-Kxx key comparison, expected start in 2023

- EMPIR proposal "STELLAR" (funding for 2020 – 2023)
  - SI-traceability and OIRS of $^{13}C/^{12}C$ ratio in CH_4



© credit to BIPM



Acknowledgements

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EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

CLIMATE AND OCEAN OBSERVATION

https://www.vtt.fi/sites/SIRS/

https://msu.euramet.org/

https://www.euramet.org/european-metrology-networks/climate-and-ocean-observation/

Have a nice time for everybody

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