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.
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
CO₂ is an important greenhouse gas

Global monthly mean CO₂

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

https://www.esrl.noaa.gov/gmd/ccgg/trends/
CO₂ is an important greenhouse gas

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

About 1.1% of CO₂ contains ¹³C isotope

Plants “prefer” ¹²C over ¹³C
Fossil fuel is depleted in ¹³C
Combustion produces CO₂ with less ¹³C

Isotopes are the key to understand sinks and sources of CO₂
Isotopic composition of CO$_2$

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

natural abundance:

\begin{align*}
^{12}\text{C} & \text{(98.9\%)} & ^{13}\text{C} & \text{(1.1\%)} & ^{14}\text{C}_{\text{(radioactive)}} \\
^{16}\text{O} & \text{(99.8\%)} & ^{18}\text{O} & \text{(0.2\%)} & ^{17}\text{O} & \text{(0.04\%)}
\end{align*}

\text{delta-value (sub-\text{\%} variations)}:

\[ \delta^{13}\text{C} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{reference}}} - 1 \]

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

\text{solids}
**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

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>Mass (u)</th>
<th>Rel. abundance $n_i/\Sigma n_j$ (mol/mol)</th>
<th>Rel. contribution to mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $^{12}$C$^{18}$O$_2$</td>
<td>44</td>
<td>$9.842 \cdot 10^{-1}$</td>
<td>100.000</td>
</tr>
<tr>
<td>2 $^{13}$C$^{16}$O$_2$</td>
<td>45</td>
<td>$1.100 \cdot 10^{-2}$</td>
<td>93.636</td>
</tr>
<tr>
<td>3 $^{12}$C$^{16}$O$^{18}$O</td>
<td>46</td>
<td>$3.947 \cdot 10^{-3}$</td>
<td>99.785</td>
</tr>
<tr>
<td>4 $^{12}$C$^{16}$O$^{17}$O</td>
<td>45</td>
<td>$7.478 \cdot 10^{-4}$</td>
<td>6.364</td>
</tr>
<tr>
<td>5 $^{13}$C$^{16}$O$^{18}$O</td>
<td>47</td>
<td>$4.413 \cdot 10^{-5}$</td>
<td>96.710</td>
</tr>
<tr>
<td>6 $^{12}$C$^{16}$O$^{17}$O</td>
<td>46</td>
<td>$8.361 \cdot 10^{-6}$</td>
<td>0.211</td>
</tr>
<tr>
<td>7 $^{12}$C$^{16}$O$_2$</td>
<td>48</td>
<td>$3.957 \cdot 10^{-6}$</td>
<td>99.578</td>
</tr>
<tr>
<td>8 $^{12}$C$^{17}$O$^{18}$O</td>
<td>47</td>
<td>$1.500 \cdot 10^{-6}$</td>
<td>3.286</td>
</tr>
<tr>
<td>9 $^{12}$C$^{17}$O$_2$</td>
<td>46</td>
<td>$1.421 \cdot 10^{-7}$</td>
<td>0.004</td>
</tr>
<tr>
<td>10 $^{13}$C$^{16}$O$^{18}$O</td>
<td>49</td>
<td>$4.424 \cdot 10^{-8}$</td>
<td>0.000</td>
</tr>
<tr>
<td>11 $^{13}$C$^{17}$O$^{18}$O</td>
<td>48</td>
<td>$1.676 \cdot 10^{-8}$</td>
<td>0.422</td>
</tr>
<tr>
<td>12 $^{13}$C$^{17}$O$_2$</td>
<td>47</td>
<td>$1.588 \cdot 10^{-9}$</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Absorption spectrum of CO$_2$ isotopologues

\[ x(\text{^{13}C}^{16}\text{O}_2) = A \frac{k_B \cdot T}{S \cdot p \cdot L} \]

Rotational-vibrational line position / cm$^{-1}$

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

- absorption inside the gas cell (CO$_2$ in air)
- $p = 100$ mbar, $T = 310$ K, $L = 5.4$ m

Thermo Scientific Delta Ray

portable optical isotope ratio spectrometer
Optical isotope ratio measurements

\[ x(^{13}C^{16}O_2) = A \frac{k_B \cdot T}{S \cdot p \cdot L} \]

\[ \frac{^{13}C}{^{12}C} = \frac{A(^{13}C^{16}O_2) S(^{12}C^{16}O_2)}{A(^{12}C^{16}O_2) S(^{13}C^{16}O_2)} \]

\[ u(S) > 1\% \rightarrow u(S) < 0.1\% \]

- More accurate line data is required (in progress @ PTB)
- Towards “Optical Transfer Standard”
**Calibration based on reference gases**

\[
\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{reference}}} = \frac{\left(\frac{A(^{13}\text{C}^{16}\text{O}_2)}{A(^{12}\text{C}^{16}\text{O}_2)}\right)_{\text{sample}}}{\left(\frac{A(^{13}\text{C}^{16}\text{O}_2)}{A(^{12}\text{C}^{16}\text{O}_2)}\right)_{\text{reference}}}
\]

\[
\delta^{13}\text{C} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{reference}}} - 1
\]

**Measurement sequence (loop)**

\[
\delta_{2,t} = \delta_{2,m} + \frac{2}{3}(\delta'_{2,m} - \delta_{2,m})
\]

\[
\delta_{1,t} = \delta_{1,m} + \frac{1}{3}(\delta'_{1,m} - \delta_{1,m})
\]

\[
\delta_{a,t} = \frac{\delta_{1,t} - \delta_{2,t}}{\delta_{1,m} - \delta_{2,m}}(\delta_{a,m} - \delta_{1,m}) + \delta_{1,t}
\]

**Reference 1**  
**Reference 2**  
**Sample**  
**Reference 1**  
**Reference 2**  
**Sample**  
**Air ref.**
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 “synthetic” air composition in place
- Mismatch in air matrices between reference and sample leads to artificial bias in $\delta$ values

Pressure broadening coefficient $\gamma_L$ is a fixed parameter in default fitting model approach (!)

- CO2-N2
- CO2-O2
- CO2-Ar

[From Brownsword1995]
[From Margottin-Maclou1988]
Matrix mismatch = broadening parameters are not appropriately adapted to the experimental situation.

<table>
<thead>
<tr>
<th></th>
<th>$\text{Ar} (%%)$</th>
<th>$\text{O}_2 (%%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{13}\text{C}$</td>
<td>0.39</td>
<td>-0.14</td>
</tr>
<tr>
<td>$\delta^{18}\text{O}$</td>
<td>-0.32</td>
<td>0.22</td>
</tr>
</tbody>
</table>

A slightly 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

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

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

| δ\(^{13}\)C | -7.94(1)‰ |
| δ\(^{18}\)O | -14.69(3)‰ |
Uncertainty budget

<table>
<thead>
<tr>
<th>Source of Uncertainty</th>
<th>Default (Factory)</th>
<th>Drift correction + Linearity calibration (400-800 ppm) + improved PTB-fit approach</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^{13}$C / ‰</td>
<td>$\delta^{13}$C / ‰</td>
</tr>
<tr>
<td>Reproducibility, $u_{repr}$</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Calibration, $u_{cal}$</td>
<td>0.06</td>
<td>0.1</td>
</tr>
<tr>
<td>Concentration dependence, $u_{conc}$</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Matrix mismatch effect, $u_{matrix}$</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>Combined standard uncertainty, $u$</td>
<td>0.10</td>
<td>0.13</td>
</tr>
<tr>
<td>Expanded uncertainty, $U (k=2, 95%$ confidence interval)</td>
<td>0.20</td>
<td>0.25</td>
</tr>
</tbody>
</table>

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

Prokhorov, I., I. Chubchenko, O. Werhahn, G. Li, and V. Ebert "Eliminating the effect of air composition in optical isotope ratio spectrometer", in preparation.
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$_4$
This study has received funding from the European Metrology Programme for Innovation and Research (EMPIR) co-financed by the EURAMET Participating States and from the European Union's Horizon 2020 research and innovation programme as of the SIRS project (16ENV06). PTB is member of the European Metrology Network for Climate and Ocean Observation.

https://www.vtt.fi/sites/SIRS/
https://msu.euramet.org/
Have a nice time for everybody