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

Isotopic composition of carbon dioxide $\delta^{13}C$ and $\delta^{18}O$ can be used to discriminate between natural and various manmade sources of $\text{CO}_2$ [1]. Within the EMPIR project “Metrology for Stable Isotope Reference Standards” (SIRS) [2,3] advanced spectroscopic methods are applied.

Introduction

\[
\delta^{13}C = \frac{^{13}r}{^{13}r_{ref}} - 1 = \frac{^{13}R}{^{13}r_{ref}} - 1
\]

\[
^{13}R = \frac{x(^{13}C^{16}O_2)}{x(^{12}C^{16}O_2)}
\]

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

Isotope ratio and “delta” value

Isotopologue ratio

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

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Light source</td>
<td>ICL</td>
<td>DFG PPLN</td>
</tr>
<tr>
<td>Center wavelength</td>
<td>4.3 µm</td>
<td>4.3 µm</td>
</tr>
<tr>
<td>Gas cell pathlength</td>
<td>36 m</td>
<td>5.4 m</td>
</tr>
<tr>
<td>Gas cell pressure</td>
<td>50 hPa</td>
<td>100 hPa</td>
</tr>
<tr>
<td>Gas cell temperature</td>
<td>294 K</td>
<td>311 K</td>
</tr>
</tbody>
</table>

Measured spectra

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

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.
Study of matrix effects

\[ w_L = \sum_i p x_i \gamma_i (m, \nu, T) \]

\(^{12}\text{C}^{16}\text{O}\) transition P(20) in 1001-1000 band

\( p = 100 \text{ hPa}, \ T = 311 \text{ K}, \ \ x\text{CO}_2 = 450 \text{ ppm} \)

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

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.
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].

- Two-stage thermal control system will be used to reach the target uncertainties of 0.1 ‰ for δ$^{13}$C-CO$_2$ and 0.5 ‰ for δ$^{18}$O-CO$_2$.


Presented at EGU General Assembly 2019, April 7-12, 2019, Vienna, Austria and The 20$^{th}$ WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2019), September 2-5, 2019, Jeju, Korea.
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-CO$_2$ measurements is around 0.1 $\%o$, at a nominal CO$_2$ mole fraction of 400 $\mu$mol 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 $\delta$-values on matrix 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.