On isotopologue-specific calibration of CO$_2$ measurements

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**Introduction - the problem**

- Gravimetric, manometric or GC -based mole fraction calibration scales are based on whole $CO_2$: isotope-independent

- Optical techniques - laser or FTIR analysers - may (or may not) determine amounts of specific isotopologues of $CO_2$ from single absorption lines or bands

Two issues:
- Isotopic composition of the calibration standards
- Calibration effects in the calculation of $\delta$ quantities
## Housekeeping

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>Notation</th>
<th>Nat Abundance</th>
<th>(X_{abc})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{12}\text{C}^{16}\text{O}_2)</td>
<td>626</td>
<td>0.98420</td>
<td></td>
</tr>
<tr>
<td>(^{13}\text{C}^{16}\text{O}_2)</td>
<td>636</td>
<td>0.01106</td>
<td></td>
</tr>
<tr>
<td>(^{12}\text{C}^{18}\text{O}^{16}\text{O})</td>
<td>628</td>
<td>0.0039471</td>
<td></td>
</tr>
<tr>
<td>(^{12}\text{C}^{17}\text{O}^{16}\text{O})</td>
<td>627</td>
<td>0.000734</td>
<td></td>
</tr>
</tbody>
</table>

- **Concentration /mole fraction:** \(C_{626}, C_{636}\ldots\)
- **Scaled by natural abundance:** \(C'_{626} = C_{626} / X_{626}, C'_{636} = C_{636} / X_{636}\)
- **Isotopic delta values:** \(\delta^{13}C = \frac{C_{636}}{X_{636}} / \frac{C_{626}}{X_{626}} - 1 = \frac{C'_{636}}{C'_{626}} - 1\)

(All values are in parts per thousand relative to the Isotope Abundance of the reference standard.)
Isotopologue amounts:
*Given* $C_{CO_2}$, what are $C_{626}$, $C_{636}$ ...?

**Total CO$_2$ :**

$$C_{CO_2} = C_{626} + C_{636} + C_{628} + C_{627} + ...$$

**then**

$$C_{626} = \frac{X_{626} C_{CO_2}}{X}$$

$$C_{636} = \frac{X_{636} (1 + \delta^{13}C) C_{CO_2}}{X}$$

**where**

$$X = X_{626} + (1 + \delta^{13}C) X_{636} + (1 + \delta^{18}O) X_{628} + ...$$

$$(X = 1.0000 \text{ for natural abundance})$$

- **Message 1:**
  To determine the individual isotopologue amounts $C_{626}$, $C_{636}$ ... the complete isotopic composition (all $\delta$s) should be known

- See also Loh et al., *GGMT Jena, 2009* -same message
Absolute isotopologue calibration

Calibration: derive calibration coeffs $a$, $b$ by regression

$$C'_{\text{626, meas}} = a_{626} C'_{\text{626, ref}} + b_{626}$$

$$C'_{\text{636, meas}} = a_{636} C'_{\text{636, ref}} + b_{636}$$

Analysis: calculate $C$ from $C_{\text{meas}}$ & calibration coeffs

$$C'_{626} = (C'_{\text{626, meas}} - b_{626}) / a_{626}$$

$$C'_{636} = (C'_{\text{636, meas}} - b_{636}) / a_{636}$$

then

$$\delta^{13}C = \frac{C'_{636}}{C'_{626}} - 1$$
Empirical $\delta^{13}C$ calibration
when a full isotopic calibration is not available

$$\delta_{\text{meas}} = \frac{C'_636,\text{meas}}{C'_626,\text{meas}} - 1$$

$$\delta_{\text{meas}} = \frac{a_{636} C'_636 - b_{636}}{a_{626} C'_626 - b_{626}} - 1$$

$$\delta_{\text{meas}} = \alpha \cdot \delta + (\alpha - 1) + \frac{\beta}{C'_626,\text{meas}}$$

$$\alpha = \frac{a_{636}}{a_{626}}$$

$$\beta = b_{636} - \alpha(\delta + 1)b_{626}$$

Scale shift
$(\alpha-1) \times 1000\%$

$1/\text{CO}_2$
dependence
Message 2

- “Absolute” calibration
  - Standards with known $[CO_2]$ and isotopic composition
  - Isotopologues calibrated independently
  - $\delta^{13}C$ calculated directly

\[
\delta^{13}C_{true} = \frac{C'_636}{C'_626} - 1
\]

- “Empirical” calibration
  - Determine $\alpha$ and $\beta$ empirically
    - $\alpha$ => scale shift
    - $\beta$ => $CO_2$ dependence
In practice - absolute calibration
FTIR calibration vs reference gases, MPI-Jena

$^{12}\text{CO}_2$
$y = 0.9735 \cdot x + 0.3902$

$^{13}\text{CO}_2$
$y = 0.9977 \cdot x - 0.7752$

$1\sigma$ repeatability: $\text{CO}_2 < 0.05$ ppm
$\delta^{13}\text{C} < 0.1\%$
Empirical calibration

\[ \delta^{13}C_{\text{meas}} = \alpha \cdot \delta^{13}C_{\text{true}} + (\alpha - 1) + \frac{\beta}{C'_\text{626,meas}} \]

CO₂ dependence

Calibration, 5 stds
CO₂-corrected

Slope = \( \beta = -1726 \, \text{‰ ppm} \)

\[ y = 1.01 \times x + 22.1 \]
In the field:
Quasom $CO_2$ soil study, FTIR, Jena

- Soil-plant-atmos. carbon exchange
- Air cycled chamber - FTIR - chamber
- Measure chamber $CO_2$ and $\delta^{13}C$ by FTIR
  - soil & plant respiration
  - 1 min average measurements
  - Chambers closed 10 minutes
- Continuous operation June 2011 - present
Chamber data

- 7 chamber sequence, 1 July 2011, 21:00-22:45
Keeling plot => source $\delta^{13}C$

- Single chamber closure, 15 min

- Blue triangles: empirical, intercept = -31.8‰
- Red diamonds: absolute, intercept = -32.1‰
Conclusions

Message 1:
To determine any one isotopologue amount $C_{626}$, $C_{636}$ ... in a standard of known total CO$_2$ mole fraction, the complete isotopic composition (all $\delta$s) should be known.

Message 2:
If isotopically characterised standards are available, isotopic ratios such as $\delta^{13}C$ can be calculated directly (“absolute “ calibration).

If not, calculation of $\delta^{13}C$ directly from uncalibrated isotopologue measurements in general leads to a scale offset and a CO$_2$ concentration dependence of $\delta^{13}C$ which must be characterised (“empirical” calibration).
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◆ Thank you