Linking Isotopologue Specific Measurements to Existing International Mole Fraction Scales

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How to calibrate?

- Instrument only sensitive to $^{12}\text{C}^{16}\text{O}^{16}\text{O}$ (& $^{12}\text{CH}_4$)
- Strictly, can only calibrate to those components
- Historically methods have measured ‘total’ CO$_2$
- Use of calibration gases with different isotopic ratios will lead to systematic (albeit small) errors in data
  - Demonstrated in two JGR papers, 2006 & 2009:

**Effect of carbon isotopic variations on measured CO$_2$ abundances in reference gas mixtures**

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**Theoretical and experimental evaluation of the isotope effect of NDIR analyzer on atmospheric CO$_2$ measurement**

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Calibration proposal

• Isotopologue = distinct molecular species
• Create primary standards for each measureable isotopologue
• Archive primary data as $^{12}$C$^{16}$O$^{16}$O (and $^{12}$CH$_4$)
• Create a secondary record that accounts for remaining isotopologues
  • Explicit measurement where feasible (e.g. $^{13}$C$^{16}$O$^{16}$O)
  • Assumptions about fractional abundance and biogeochemical cycles
• This secondary record should be comparable with current data

• Why do it this way?
  • Clearer where the uncertainties are
  • As it becomes possible to measure additional isotopologues, these can be accommodated naturally in the record
Calibration strategy #1: isotopically pure gases

1. Prepare a new calibration suite from isotopically pure gas samples ($^{12}$C) in zero air.
2. Measure [CH$_4$] and [CO$_2$] on GC to tie to pre-existing scales.
3. Assume GC response is isotopologue independent.
4. Use these data to check the Picarro isotopos instrument $^{13}$CO$_2$ response and confirm $^{12}$CO$_2$ response is zero.
5. Check against LoFlo and other calibrations suites that have been characterised for total [CO$_2$] and on IRMS.
6. Use these data to calibrate Picarro CO$_2$/CH$_4$ response in $^{13}$CH$_4$ & $^{12}$CO$_2$ domains.
7. Measure [CH$_4$] and [CO$_2$] on both cavity ringdown instruments.
8. Use calibrated Picarro CO$_2$/CH$_4$ to transfer the $^{13}$C scale in both CH$_4$ and CO$_2$ to working air standards.
Isotopically pure standards

• Isotopically pure standard created in-house

• GC measurement determines CO$_2$ value

• Assume since isotopically pure material was used, GC numbers are $^{12}$C numbers

• Calibrate Picarro to the isotopically pure standard

• Check Picarro measurements of other tanks are lower than the known concentrations for ‘total CO$_2$’ and ‘total CH$_4$’ by the expected amount
  - can be calculated with IRMS measurement of $\delta^{13}$C/ $\delta^{18}$O for calibration gas
Calibration strategy #2: partitioning the total CO₂

- Assume GC isotopologue independent
- GC & IRMS: total CO₂ partitioned into three major isotopologues

\[ ^{12}\text{C}^{16}\text{O}^{16}\text{O} = \alpha; \]
\[ ^{13}\text{C}^{16}\text{O}^{16}\text{O} = \beta; \]
\[ ^{12}\text{C}^{18}\text{O}^{16}\text{O} = \gamma; \]

\[ \text{GC}[\text{CO}_2] = \text{TOT}_- \text{CO}_2 = \kappa \approx \alpha + \beta + 2\gamma \]

\[ r^{13} \approx \frac{^{13}\text{C}^{16}\text{O}^{16}\text{O}}{^{12}\text{C}^{16}\text{O}^{16}\text{O}} = \frac{\beta}{\alpha} \]

\[ r^{18} \approx \frac{^{12}\text{C}^{18}\text{O}^{16}\text{O}}{^{12}\text{C}^{16}\text{O}^{16}\text{O}} = \frac{\gamma}{\alpha} \]

\[ \delta^{13}\text{C}_{\text{VPDB, CO}_2} = \left[ \frac{r^{13}}{r^{13}} - 1 \right] \times 10^{3}; \]

\[ r^{13} = r^{13}_{\text{VPDB, CO}_2} = 0.011237200; \]

\[ r^{13} = r^{13}_{\text{VPDB, CO}_2} \left[ \left( \delta^{13}\text{C}_{\text{VPDB, CO}_2} \times 10^{-3} \right) + 1 \right] = \epsilon \]

\[ \delta^{18}\text{O}_{\text{VPDB, CO}_2} = \left[ \frac{r^{18}}{r^{18}} - 1 \right] \times 10^{3}; \]

\[ r^{18} = r^{18}_{\text{VPDB, CO}_2} = 0.002088349; \]

\[ r^{18} = r^{18}_{\text{VPDB, CO}_2} \left[ \left( \delta^{18}\text{O}_{\text{VPDB, CO}_2} \times 10^{-3} \right) + 1 \right] = \phi \]

\[ \alpha = \frac{\kappa}{1 + \epsilon + 2\phi}; \beta = \frac{\epsilon\kappa}{1 + \epsilon + 2\phi}; 2\gamma = \frac{2\phi\kappa}{1 + \epsilon + 2\phi} \]
LoFlo/Picarro ambient record in an urban environment

- Rigorous test – dirty and highly variable environment
- Missing data are periodic calibrations and tank measurements
- Picarro data lower than LoFlo data
Picarro calibration

- Based on the suite of CSIRO GASLAB laboratory standards that are tied to the LoFlo 2b instrument.

- These tanks have been measured at NOAA and are on the WMO07x scale.

- All seven tanks (span 320 – 460 ppm) were produced from ambient air and are isotopically identical to within 0.5‰

- MAT252 measurements of $\delta^{13}C$ and $\delta^{18}O$ are used to extract $^{12}CO_2$ fraction

- Picarro calibrated to $^{12}CO_2$ fraction.
Picarro calibration to $^{12}\text{CO}_2$ fraction of LoFlo2b laboratory primary suite

- Picarro response function linear over 320 – 460 ppm

- Picarro calibrated to $^{12}\text{CO}_2$ fraction
  - Picarro measurement should be ~1.5% lower than LoFlo measurement
Hourly matched data

Expected difference = -1.5%
Mean difference = -1.48 ± 0.07%
Conclusions

• Sound metrology suggests we should calibrate isotopologue specific measurements to an isotopologue specific scale

• Such an approach:
  • eliminates systematic errors associated with variable isotopic composition of calibration standards
  • requires linkages to current mole fraction scales

• Two complementary strategies have been described
• One strategy has been implemented in an overlap experiment with a LoFlo NDIR instrument