Improved CRDS $\delta^{13}C$ Stability Through New Calibration Application For CO_2 and CH_4

PICARRO

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Abstract

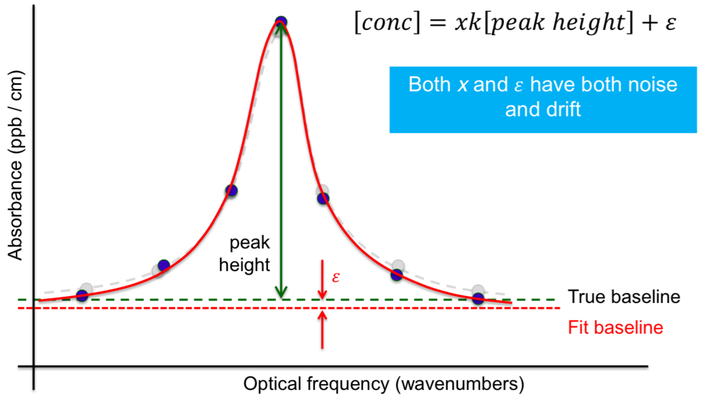
Stable carbon isotope ratio measurements of CO2 and CH4 provide valuable insight into global and regional sources and sinks of the two most important greenhouse gasses. Methodologies based on Cavity Ring-Down Spectroscopy (CRDS) have been developed capable of delivering δ13C measurements with a precision greater than 0.12 permil for CO2 and 0.4 permil for CH4 (1 hour window, 5 minute average). Here we present a method to further improve this measurement's stability. We have developed a two point calibration method which corrects for δ13C drift due to a dependance on carbon species concentration. This method calibrates for both carbon species concentration as well as δ13C. We go on to show that this added stability is especially valuable when using carbon isotope data in linear regression models such as Keeling plots, where even small amounts of error can be magnified to give inconclusive results. This method is demonstrated in both laboratory and ambient atmospheric conditions, and we demonstrate how to select the calibration frequency.

Background: CRDS Drift

Error Analysis in $\delta^{13}C$ Measurements

$$[conc] = xk[peak\ height] + \varepsilon$$

Both x and ε have both noise and drift



$$\delta_{13} = 1000\left(\frac{r_{sample}}{r_{VPDB}} - 1\right) \qquad r_{sample} = c_{13}/c_{12}$$

$$\delta_{true} = 1000\left(\frac{(x_{13}k_{13}m_{13} + \varepsilon_{13})/(x_{12}k_{12}m_{12} + \varepsilon_{12})}{r_{VPDB}} - 1\right)$$

Ignore ε_{12} when $m_{13} \ll m_{12}$, and $x_{13} \sim x_{12} \sim 1$

$$\delta_{true} = 1000\left(\begin{array}{l} \dfrac{k_{13}m_{13}/k_{12}m_{12}}{r_{VPDB}} - 1 \\ +\left(\dfrac{x_{13}}{x_{12}} - 1\right)\dfrac{k_{13}m_{13}/k_{12}m_{12}}{r_{VPDB}} \\ +\varepsilon_{13}/x_{12}k_{12}m_{12}r_{VPDB} \end{array}\right)$$

δ_{raw}

Delta span drift

[concentration]$^{-1}$ drift

Define: $\Delta_H \equiv \delta_{HI} - \delta_{HI\ raw}$ and $\Delta_L \equiv \delta_{LO} - \delta_{LO\ raw}$

$$A_i = \left[\frac{\Delta_H(\delta_{LO\ raw} + 1000) - \Delta_L(\delta_{HI\ raw} + 1000)}{\dfrac{(\delta_{LO\ raw} + 1000)}{C_H} - \dfrac{(\delta_{HI\ raw} + 1000)}{C_L}}\right]_i$$

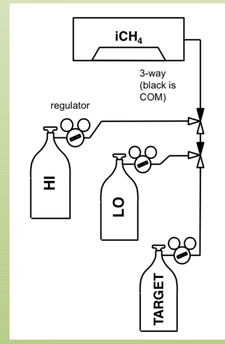
$$B_i = [(\Delta_H - A_i/C_H)/(\delta_{HI\ raw} + 1000)]_i$$

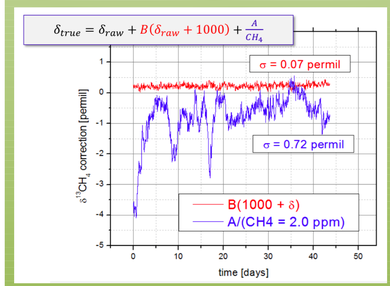
$$\delta_{true} = \delta_{raw} + B(\delta_{raw} + 1000) + \frac{A}{^{12}CH_4}$$

Experimental

Instrument Calibration Proof of Concept

- Isotopic standards were obtained from Isometric Instruments.
- Perform a concentration calibration prior to an isotopic calibration.
- In order to tease out the concentration effect on the isotope measurement, select a large span between HI concentration and LO concentration (For methane, 1.8 ppm to 10 ppm; for carbon dioxide, 390 ppm to 1000 ppm.
- Target tank was selected based on expected concentration of field measurements.



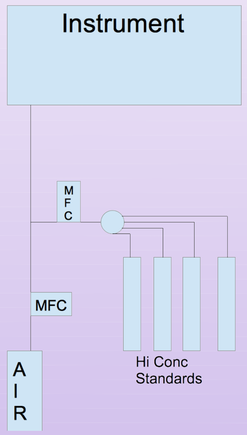


Post Processing:

- Use the HI and LO data to calculate the two error coefficients, A and B.
- From target data, we see that A dominates the isotopic correction.
- Upwards of 90% of the correction can be attributed to A, implying that a 1 tank calibration could be used if space or resources are limited.

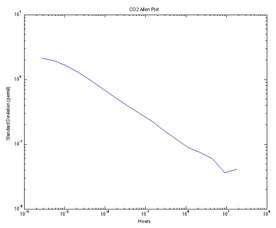
Verify Unknown Tanks for Field Calibrations

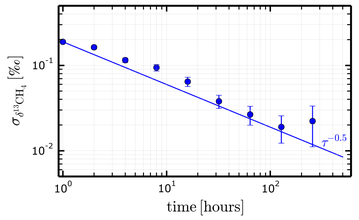
- **Instrument Calibration**
  - 4 isotopic standards were obtained from Isometric Instruments
  - Using zero air and mass flow controllers, each bottle can be cycled through at varying concentrations.
  - In this scheme, unknown tanks can be given verified concentration and isotopic certification.
  - Later, these tanks will be deployed to the field for on site calibrations.
  - For our study, a needle valve was used to control dilution flow. However, a mass flow controller (MFC) would be better suited for the job.
  - As seen below, multiple instruments can run this scheme simultaneously, allowing for instrument comparison and validation



Results

Precision Only Limited By Time



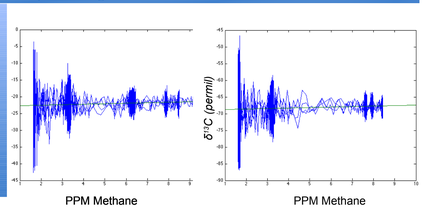


Allen Variance Plots

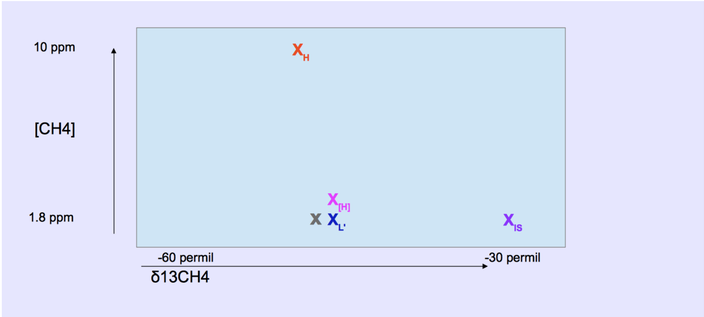
The above plots show the standard deviation of the measurements as a function of the averaging time. By using our drift correction the only noise left in the measurement is white noise. Hence, as averaging time increases, measurement noise decreases. Simply select the precision required and average over the corresponding time.

Isotope Response to Concentration

The right two plots show an instrument's response to changes in concentration while measuring at a constant $\delta^{13}C$. In both instances the slope of the best fit was 0.142 permil/ppm, showing that corrections derived from one value of $\delta^{13}C$ are valid across the range of $\delta^{13}C$ measurements



Recommended Calibration Scheme



Use Four Tanks

- X_H: High concentration, ambient isotope.
- $X_{[H]}$: Concentration should be highest expected measurement. Used for conc cal only.
- X_L: Low concentration, ambient isotope. Used for conc and isotope calibration.
- X_{IS}: Target tank. Used to check all calibrations.

Schedule

- After 90 minutes of sampling, run X_H and X_L. Calculate error coefficients A and B, and apply isotope corrections.
- Every 23 hours, run $X_{[H]}$. Use this data, along with the most recent data from X_L to perform a concentration calibration.
- Every 23 hours, run X_{IS} and use this data to test all calibrations.

Conclusions and Recommendations

In this study, we have demonstrated a new method for correcting drift in stable carbon isotope measurements. This drift is dependent on the carbon species concentration, and is corrected for using two error coefficients, A and B. These coefficients are calculated from data from two standards, HI and LO. These standards should be measured frequently, roughly every 90 minutes. When this correction is run the measurement is stable such that increasing the averaging period can decrease the noise well below 0.1 permil.

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