

## ***Interactive comment on “Evaluating calibration strategies for isotope ratio infrared spectroscopy for atmospheric $^{13}\text{CO}_2/^{12}\text{CO}_2$ measurement” by X.-F. Wen et al.***

**P. Sturm (Referee)**

sturm@tofwerk.com

Received and published: 5 March 2013

### General Comments

This paper compares two commercial analyzers for  $\delta^{13}\text{C}$ - $\text{CO}_2$  measurements and evaluates different calibration strategies. The comparison is based on laboratory tests using three different calibration gases and a 7-day measurement of atmospheric air. Four different calibration approaches for the isotope ratio are considered:

1. Calibrating the  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  isotopologues individually using 2-point gain and offset calibrations.

C170

2. Calibrating the isotope ratio using two individual 1-point gain calibrations, which are then averaged with weights according to the  $^{12}\text{CO}_2$  concentration of the two standard gases to reduce errors from analyzer nonlinearities.
3. Calibrating the isotope ratio using a 2-point gain and offset calibration.
4. Calibrating the isotope ratio using a 1-point offset calibration.

The authors raise some important questions here. Precise and accurate measurements of isotope ratios are challenging and isotope ratio analyzers can only provide high-quality data in combination with a proper calibration strategy. It is not obvious, which calibration method should be used and a number of calibration approaches and post-processing procedures have been reported so far, due to different analyzer characteristics and the different applications of the measurements. The authors empirically compare four different methods, but they could further strengthen the manuscript by a more detailed discussion of the underlying assumptions and limitations of the different models. For example, the discussion about the concentration dependence deserves some more attention. If we assume that the analyzers measure the isotopologue mole fractions independently and that the response is linear, i.e., that the relationship between measured ( $c_{\text{measured}}$ ) and true ( $c_{\text{true}}$ ) isotopologue mole fractions can be described as

$$c_{12,\text{true}} = a_{12} \cdot c_{12,\text{measured}} + b_{12}, \quad (1)$$

$$c_{13,\text{true}} = a_{13} \cdot c_{13,\text{measured}} + b_{13} \quad (2)$$

with  $a$  and  $b$  the gain and offset coefficients, then it is worth emphasizing a few additional points.

If  $b_{12} \neq 0$  and/or  $b_{13} \neq 0$ , then an “apparent” concentration dependence of the  $\delta^{13}\text{C}$  will be measured when a gas with constant  $\delta^{13}\text{C}$  at varying  $\text{CO}_2$  mole fractions is analyzed (see Griffith et al., 2012, AMT). This apparent concentration dependence does not

C171

originate from any spectroscopic effect, but is simply a result of taking the ratio of two linear variables. The measured and true delta value will be related according to:

$$\delta_{\text{true}} = \frac{a_{13}c}{a_{12}c + b_{12}} \delta_{\text{measured}} + \frac{(a_{13} - a_{12})c + b_{13} - b_{12}}{a_{12}c + b_{12}} \quad (3)$$

where  $c$  is the measured  $^{12}\text{CO}_2$  mole fraction.

Method 1 has the advantage that one does not have to deal with this apparent concentration dependence. If a delta value calibration (e.g. method 3) is used, however, then this definitely needs to be taken into account.

Method 2 is a somewhat unusual approach which so far has been used by the authors only for water vapor isotope measurements. It seems that this method consists of two 1-point calibrations rather than a true 2-point calibration, because only the gain of the isotope ratio is measured. This means that one has to assume that there is no offset in the calibration (i.e. that the analyzers are “zeroed” well). If this is not the case, then method 2 might not give reliable results, although part of the bias will be corrected by averaging the two calibrations.

Method 3, as it is presented here, also only works if there is no offset in the calibration (i.e. measurement of a zero gas will yield zero,  $b_{12} = b_{13} = 0$ ). Otherwise an apparent concentration dependence appears. The concentration dependence can be corrected if it is measured. Unfortunately, this has not been done here and I suspect that part of the discrepancy to the other calibration approaches is based on this.

There are instruments that show a “real” concentration dependence of the isotope ratio even when they are properly zeroed (see e.g. Tuzon et. al, 2008, Appl. Phys. B), meaning that the assumption of independence and linear response of the isotopologue mole fractions is not exactly true. In this case, method 3 still provides a straightforward way to calibrate if the concentration dependence corrected delta value is used.

Finally, method 4 is a simplification of method 3 as it assumes that the delta value gain

C172

is constant and exactly 1 and it only performs an offset correction. Without a concentration dependence correction it also has to assume that the isotopologue offsets are zero (as in method 3). Therefore, method 4 can actually only be expected to perform well with a perfect analyzer, where the measured delta value is equal to the true value.

In addition to these general comments the authors might also consider the following specific remarks.

#### Specific Comments

P. 796 line 11: The absolute value of the difference before calibration does not tell much if it is merely based on the pre-defined internal calibration factors of the analyzers. I would not mention it in the abstract. These factors are very likely different for every analyzer and depend on the quality of the factory pre-calibration. Depending on the calibration method, these internal coefficients may influence the apparent concentration dependence, so it might be advantageous to set them properly, however, in the end the relevant figure is the difference after the calibration.

P. 797 line 7: Fundamentally, IRMS is prone to artifacts too. However, the difference to IRIS probably is, that IRMS labs are used to deal with them and have developed procedures to account for them, while still less such procedures exist for IRIS and some users of IRIS might not yet be fully aware of them.

P. 797 line 24: What means absolute and empirical here? I think all calibrations are empirical rather than absolute in the sense that they rely on empirically derived calibration factors and correction functions. Griffith et al., 2012 have used the term “empirical” for method 3 when additionally the apparent  $\text{CO}_2$  dependence is corrected. Method 3 in this paper does however not include such a correction.

P. 798 line 5: Explain what you mean with “to minimize the delta-stretching effect”. I don’t think method 3 minimizes any delta-stretching effect.

P. 799 line 1: How much does the pressure broadening, which was not corrected, affect

C173

the Picarro data? There are other potential artifacts, too. Spectral interference with water vapor (up to 5‰ according to Picarro, Rella, 2012a) or CH<sub>4</sub> (0.4‰/ppm, Vogel et al., 2013, AMT) can also have a large effect on δ<sup>13</sup>C. Was this taken into account? And what is the uncertainty of the water dilution correction? All this makes it quite possible, that the difference between the two analyzers is not just due to CO<sub>2</sub> concentration effects, but also due to biases from spectral broadening and interferences.

P. 800 line 5: I suggest avoiding the extraneous numerical factor 1000 in equations 3b, 3c and 4. The isotope delta is a dimensionless quantity and the factor 1000‰ (which is 1) is not needed for a coherent definition of the isotope δ value (e.g. see Coplen, 2011, Rapid Commun. Mass Spectrom).

P. 800 line 10: What is the uncertainty in [CO<sub>2</sub>] coming from the assumption that *f* is constant, i.e. that δ<sup>18</sup>O is constant?

P. 800 line 18-20: This advantage also applies for method 3 and 4.

P. 800 line 22: change to “the calibrated ratio of carbon dioxide molar mixing ratios”

P. 800 line 23: I suggest to use R<sub>1,t</sub> instead of R<sub>1</sub> and R<sub>2,t</sub> instead of R<sub>2</sub> to be consistent with the equations of the other methods.

P. 801 line 12-14: All methods assume that the measured quantity (delta value or isotopologue mole fraction) is linearly dependent on its true value. Otherwise a 2-point calibration would not be possible. Likewise, also method 1 and 4 assumes independence of the mixing ratios.

P. 801 line 16: To be consistent with method 1, you could also present the equations of method 1 in the form  $y = m \cdot x + b$  with a gain and offset coefficient.

P. 802 line 11: Eq. 11 for the delta value is basically method 3 with  $m = 1$ , i.e., unity gain, but some offset, while Eq. 12 for CO<sub>2</sub> is method 3 with  $b = 0$ , i.e., non-unity gain, but no offset. Why do you treat the calibration differently for δ<sup>13</sup>C and CO<sub>2</sub>?

C174

P. 802 line 23: change to “NOAA-ESRL”

P. 804 line 7: change to “random white noises” (also in the caption of Fig. 1).

P. 804 line 16: Your values are typical if you compare the best precision irrespective of the averaging time. However, I would argue that 0.05‰ in 10 s is an order of magnitude more precise than 0.05‰ in 1000 s (which would roughly correspond to 0.5‰ in 10 s).

P. 805 line 11: change to “was interpolated”.

P. 805 line 25: Methods 3 and 4 also only require that the δ<sup>13</sup>C is known. Is this really a big advantage? I am not sure how valuable a calibration gas would be where only the δ<sup>13</sup>C but not the CO<sub>2</sub> mole fraction has been precisely determined. What application would only require isotope data without concentration data?

P. 806 line 10: The difference between the other calibration pairs (1.5 and 1.2‰) is also quite small compared to the measurement uncertainty. Standard gases with a larger difference (~ 10‰) would most likely reduce the calibration error of method 3.

P. 807 line 15: What is the effect on δ<sup>13</sup>C?

P. 807 line 20-21: I suspect this is because method 2 is a 1-point gain calibration, which assumes that there is no offset. If one analyzer is zeroed well, then the difference between the two methods would be smaller compared to an analyzer with large offsets. Are the offset coefficients from method 1 smaller for the Picarro analyzer than for the LGR analyzer? If so, this would confirm this explanation.

P. 808 line 16: Why did domestic heating end on 18 March? It seems unlikely that domestic heating abruptly ends from one day to the next.

P. 808 line 26: Did you correct the H<sub>2</sub>O-dependence of the Picarro data (Fig. 3b)? If not, the Picarro CO<sub>2</sub> data, which obviously is not accurate at all, rather than the δ<sup>13</sup>C data could probably explain the difference in the intercepts between the two analyzers.

P. 823: Change the y-axis label to “Keeling plot intercept (‰)”.

C175

