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Atmospheric
Measurement
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Discussions

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

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Response to the reviewer (P. Sturm)

General Comments

1) 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

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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 (cmeasured) and true (ctrue) isotopologue mole fractions can be described as

c12,true = a12*c12,measured + b12 (1)

c13,true = a13*c13,measured + b13 (2)

with a and b the gain and offset coefficients, then it is worth emphasizing a few additional points. If b12≠0 and/or b13≠0, then an "apparent" concentration dependence of the δ13C will be measured when a gas with constant δ13C at varying CO2 mole fractions is analyzed (see Griffith et al., 2012, AMT). This apparent concentration dependence does not 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:

δtrue=a13*c/(a12*c+b12)*δmeasure+((a13-a12)*c+b13-b12)/(a12*c+b12) (3)

where c is the measured 12CO2 mole fraction.

Thank you for this insightful analysis. In response, we have added the following text in Section 2.2. "The following calibration procedures aim to calibrate the IRIS measurements to the international standard and to remove concentration dependence. Because they were implemented frequently enough, they should also be able to remove instrument time drifts. Two sources can contribute to concentration dependence. In the case that the analyzer's measurements of the 12CO2 and 13CO2 molar mixing ratio are linear, an apparent concentration dependence of the δ13C will arise if the analyzer's signal intercept is nonzero (e.g. Griffith et al., 2012; Sturm, 2013). In some cases, the instrument may not be perfectly linear with respect to the mixing ratio of the individual isotopologue (e.g. Tuzson et al., 2008; Lee et al. 2005); the nonlinearity may be negligibly small for the mixing ratio measurements but may cause unacceptably large concentration dependence of the delta measurement."

2) 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.

We agree. In response, we have added this sentence to section 2.2: "If the analyzer's mixing ratio measurements are linear, Method 1 will eliminate the delta concentration dependence."

3) 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 2 is based on the assumption that the delta bias is linearly dependent on the mixing ratio. For the range of variations seen in the ambient conditions, this is a reasonable assumption. We have added the following text to improve the clarity: "This method assumes that over the measurement range, the concentration dependent behavior can be described by a linear relationship to the measured mixing ratio of the major isotopologue. . .Mathematically, if the calibrated mixing ratio and the true mixing ratios of the standards and are used in place of the measured mixing ratios , and , this method will yield identical results to Method 1."

4) 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, b12 = b13 = 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.

We did not perform the additional corrections for concentration dependence because we wanted to learn how this factory-recommended procedure compare with Methods 1 and 2. Indeed, without the corrections suggested by the reviewer, this method was not satisfactory (Table 1). We have added the following text: "Method 3 is often used in IRMS measurements to correct delta bias errors. In the case of IRIS, it works if the analyzer's mixing ratio measurements are perfectly linear and there is no offset in its calibration. Otherwise an apparent concentration dependence would still exist."

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

This is a good point. We now point out: "Method 4 is a simplification of Method 3 as it assumes that the gain factor m = 1 (Eq. 8) and only an offset correction is needed."

Specific Comments 1) 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.

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We have deleted this wording “differed by 9.44±1.65‰ (mean±1 standard deviation of hourly values) before calibration and” in the abstract.

2) 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.

We agree. We now have the following text in the Introduction: “In comparison to IRMS whose operational procedures are mature, however, IRIS is a relatively immature technology still subject to a number of artifacts some users may not be fully aware of (Griffith et al., 2012; Werner et al., 2012).”

3) 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 CO2 dependence is corrected. Method 3 in this paper does however not include such a correction.

Rewriteen as “The four in-deployment calibration methods we have examined (section 2.2) rely on empirical correction functions (e.g. Griffith et al., 2012).”

4) 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.

Deleted “to minimize the delta-stretching effect”.

5) P. 799 line 1: How much does the pressure broadening, which was not corrected, affect the Picarro data? There are other potential artifacts, too. Spectral interference with water vapor (up to 5‰to Picarro, Rella, 2012a) or CH4 (0.4 ‰ppm, Vogel et al., 2013, AMT) can also have a large effect on 13C. 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 CO2 concentration

effects, but also due to biases from spectral broadening and interferences.

In response, we have added the following text in Section 3.3: "…We were able to correct the dilution effect using the water vapor concentration measured by the analyzer but was unable to remove the effect due to the water vapor pressure broadening and the HDO spectral interference (Rella et al., 2012a; Nara et al., 2012). These latter effects are on the order of 2 ppm / %v water at 400 ppm of carbon dioxide, and can be up to 5‰ at ambient humidity (Rella et al., 2012a, 2012b)."

6) 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 value (e.g. see Coplen, 2011, Rapid Commun. Mass Spectrom).

Corrected.

7) P. 800 line 10: What is the uncertainty in [CO2] coming from the assumption that f is constant, i.e. that 18O is constant?

We now note this assumption and point out it is not a concern.

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

Clarified as . "(This advantage also applies to Method 3 and 4.)"

9) P. 800 line 22: change to "the calibrated ratio of carbon dioxide molar mixing ratios"

This change has been made.

10) P. 800 line 23: I suggest to use R1;t instead of R1 and R2;t instead of R2 to be consistent with the equations of the other methods.

These changes have been made.

11) 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.

In response to this query, we now have additional explanation for each method: Method 1: “If the analyzer’s mixing ratio measurements are linear, Method 1 will eliminate the delta concentration dependence.” Method 2: “This method assumes that over the measurement range, the concentration dependent behavior can be described by a linear relationship to the measured mixing ratio of the major isotopologue.” Method 3: “Method 3 is often used in IRMS measurements to correct the delta biases. In the case of IRIS, it works if the analyzer’s mixing ratio measurements are perfectly linear and there is no offset in its calibration. Otherwise an apparent concentration dependence would still exist.” Method 4: “Method 4 is a simplification of Method 3 as it assumes that the gain factor m = 1 (Eq. 8) and only an offset correction is needed.”

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

This change has been made.

13) 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 CO2 is method 3 with b = 0, i.e., non-unity gain, but no offset. Why do you treat the calibration differently for 13C and CO2?

This point is now noted. Mathematically the two calibrations are equivalent: correction to the molar ratio R (as in the CO2 mixing ratio) can be achieved by adding an offset to the delta value according to the Taylor approximation.

14) P. 802 line 23: change to “NOAA-ESRL”

The change has been made.

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

Changes have been made.

16) 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‰$\in 10 sisanorderofmagnitudemoreprecisethan 0.05\ in 1000 s (whichwouldroughlycorrespondto 0.5\ in 10 s)$

Rephrased as: “Our precision values are in the reported range of IRIS instruments for δ13C.”

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

Change has been made.

18) P. 805 line 25: Methods 3 and 4 also only require that the 13C is known. Is this really a big advantage? I am not sure how valuable a calibration gas would be where only the 13C but not the CO2 mole fraction has been precisely determined. What application would only require isotope data without concentration data?

Clarified. “Method 1 requires that the CO2 mixing ratio and δ13C of the calibration gases be known precisely, while Method 2 requires that δ13C be known precisely. Calibration gases supplied by local vendors often have a concentration accuracy certified to 1%; After their 13C has been analyzed by IRMS, these gases can be used for Method 2 but may not be good enough for Method 1.”

19) 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.

We now note: “To improve the measurement would require standard gases with a larger delta difference (10‰.”

20) P. 807 line 15: What is the effect on 13C?

We now note: “These latter effects are on the order of 2 ppm / %v water at 400 ppm of carbon dioxide, and can be up to 5‰ at ambient humidity (Rella et al., 2012a, 2012b).”

21) 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.

Using Method 1, the offsets were indeed smaller for Picarro than for LGR. According to the laboratory test, the Picarro analyzer's offset (mean±std) was 0.4254±0.1892 (12C) and -0.0051±0.0085 ppm (13C). The Los Gatos analyzer's offset was -1.7801±0.2827 (12C) and -0.0524±0.0046 ppm (13C). However, we are not sure if this can fully explain the difference shown. Method 2 is a linear approximation to your Eq. 3; it does not make the assumption that the analyzer's offset is zero. We have now added the following explanation: "The difference may originate from the different assumptions used by these methods: Method 1 assumes that the mixing ratios of the individual isotopologues are linear whereas Method 2 assumes that the measured delta value is linear with respect to the measured mixing ratio of the major isotopologue."

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

Clarified as: "domestic central heating (by coal and natural gas) in Beijing ended on March 18 (DOY 78) in 2012 as mandated by the city government."

23) P. 808 line 26: Did you correct the H2O-dependence of the Picarro data (Fig. 3b)? If not, the Picarro CO2 data, which obviously is not accurate at all, rather than the 13C data could probably explain the difference in the intercepts between the two analyzers.

"We were able to correct the dilution effect using the water vapor concentration measured by the analyzer but was unable to remove the smaller effect due to the water vapor pressure broadening and the HDO spectral interference (Rella et al., 2012a; Nara et al., 2012)."

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

Change has been made. Thank you.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 795, 2013.