

1 Review of:

2 **Calibration of isotopologue-specific optical trace gas** 3 **analysers: A practical guide**

4 by David W. T. Griffith

5 **General comments:**

6 The manuscript is well written and very helpful for someone anyone working with isotopologue-
7 specific optical trace gas analysers. Calibrating such instruments (or understanding the calibration)
8 is a crucial element in this field and it fits well that this guide is published to bring everybody on the
9 same page in this growing community. An important point is flawless calculations in this guide (I
10 cannot find any) which was taken serious by the author by discussing/checking the calculations
11 with several other experts in the field – as stated in the acknowledgement. In summary, this is a
12 useful guide and is recommended to be published after a revision.

13 I have one major comment that regards the comparison of the two different ways to calibrate optical
14 instruments and the suggestions made in this regards.

15 The few minor comments I have are mainly clarifications/deeper explanations about the underlying
16 idea/calculations. The manuscript has an appreciated educational character and seems also to aim on
17 students, so it might be worth to elaborate the mathematical idea a bit more at some points.

18 **Major comment:**

19 The author recommends using the “direct calibration by isotopologues amounts” due to its apparent
20 advantages (no pressure dependence, the need of only one reference gas in different “dilutions”) as
21 opposed to the calibration via different reference gases with different δ -value (“Calibration by delta
22 values”). I think this recommendation can only be done if the targeted precision in δ -value is not
23 exceeding the precision of the absolute concentrations of the reference gas and its “dilutions”. For
24 example, the precision of CO₂ absolute concentration in reference gases from international
25 reference labs is around 0.07 ppm¹. The same type of labs can provide the $\delta^{13}\text{C}(\text{CO}_2)$ in such gases
26 using IRMS with a precision in the 0.02‰ range or better, while this δ -value is relative to a material
27 with a specific isotopic composition (reference material) and therefore independent of the absolute
28 concentration of CO₂ in that gas. The 0.02‰ in $\delta^{13}\text{C}(\text{CO}_2)$ corresponds to a precision in absolute
29 concentration of about 0.008 ppm (for a 400 ppm concentration gas), so about one order of
30 magnitude better than the absolute concentration actually can be known (in absolute, SI-traceable
31 fashion).

32 As far I understand the recommended calibration approach, it ultimately depends on the precision of
33 the absolute CO₂ concentration of the used gases. Since the current limit of these values is around
34 0.07 ppm, the corresponding precision in $\delta^{13}\text{C}(\text{CO}_2)$ cannot be better than about 0.2‰ (exceptions
35 exist if the measured value is very close to the used reference gas in the calibration). If the user
36 dilutes its reference gas in a self-made experiment, it’s very likely that the dilution process will
37 introduce additional uncertainty making the in $\delta^{13}\text{C}(\text{CO}_2)$ precision (and obviously also the
38 precision of the absolute CO₂ concentration) worse.

39 This disadvantage of the “direct calibration by isotopologues amounts” has to be addressed in the
40 manuscript and the suggestion has to be adapted accordingly. A 0.2‰ in $\delta^{13}\text{C}(\text{CO}_2)$ is one order of
41 magnitude above the GAW recommendations² for which reason the proposed calibration method
42 seems not applicable for instruments applied in the context of GAW. Some of the references used in
43 the manuscript as an example of the alternative “Calibration by delta values” are used in the GAW
44 context with corresponding precision targets. So the context of these references has to be
45 reconsidered.

46 **Minor comments:**

47 -Clumped isotopes are mentioned a few times in the manuscript, but there is no example of it. It
48 would be nice to have an example for the uneducated reader. In general, one could consider to
49 extend table 2 with all 18 (or 12 distinct) possible isotopologues as an overview and list its
50 abundances (as much as known) as an overview.

51 -Page 4, line 2 and following formulas: you shorten from $n(^{12}\text{C})$ to ^{12}C . I recommend to not do this
52 because it complicates the comparison with the previous formulas and the shortening is only used in
53 the following formulas (as much I can see).

54 -Page 4, line 11-16: This section is not very clear to me. You only take 4 distinct isotopologues into
55 consideration, but R_{sum} seems to be the sum of all 18 (according to the current text). Or how do I
56 have to understand this? R_{sum} seems to be a rather abstract parameter, or does it have any easy-
57 understandable meaning?

58 -Page 7, line 35 and following: IRMSs can also be used to measure absolute abundances of the
59 single isotopologues, but the measurement is in general noisy and very difficult to calibrate. This
60 “absolute” approach has been used in the beginning of mass spectrometry before it has been
61 realized that a relative measurement with IRMS is much more precise than an absolute
62 measurement³. This is also the case for isotopologue-specific optical systems. The noise in a line
63 ratio is much smaller than the noise of the individual lines because there is a lot of
64 correlated/technical noise on two simultaneously measured lines which cancels out in a ratio (given
65 that the instrument can measure the targeted lines simultaneously in real-time as possible e.g. with a
66 direct absorption spectrometer). It’s not due to the nature of IRMS that the community has
67 converged to go for relative δ -scales, but rather due to the more fundamental analytical advantage
68 of measuring relative values with respect to a reference material as opposed to absolute
69 measurements.

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71 **References:**

- 72 1. Zhao CL, Tans PP. Estimating uncertainty of the WMO mole fraction scale for carbon
73 dioxide in air. *J Geophys Res Atmos.* 2006;111(8):1-10. doi:10.1029/2005JD006003
- 74 2. WMO. 18th WMO/IAEA meeting on carbon dioxide, other greenhouse gases and related
75 measurement techniques (GGMT-2015). *GAW Rep No 229.* 2016;(229):13-17.
76 https://library.wmo.int/opac/doc_num.php?explnum_id=3074.
- 77 3. Criss RE. *Principles of Stable Isotope Geochemistry.* Oxford University Press; 1999.
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