Review of Griffith amt 13. August 2018

Review of:

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

by David W. T. Griffith

General comments:

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

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

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

Major comment:

The author recommends using the “direct calibration by isotopologues amounts” due to its apparent advantages (no pressure dependence, the need of only one reference gas in different “dilutions”) as opposed to the calibration via different reference gases with different $\delta$-value (“Calibration by delta values”). I think this recommendation can only be done if the targeted precision in $\delta$-value is not exceeding the precision of the absolute concentrations of the reference gas and its “dilutions”. For example, the precision of CO$_2$ absolute concentration in reference gases from international reference labs is around 0.07 ppm$^1$. The same type of labs can provide the $^{\delta^{13}}$C(CO$_2$) in such gases using IRMS with a precision in the 0.02‰ range or better, while this $\delta$-value is relative to a material with a specific isotopic composition (reference material) and therefore independent of the absolute concentration of CO$_2$ in that gas. The 0.02‰ in $^{\delta^{13}}$C(CO$_2$) corresponds to a precision in absolute concentration of about 0.008 ppm (for a 400 ppm concentration gas), so about one order of magnitude better than the absolute concentration actually can be known (in absolute, SI-traceable fashion).

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

This disadvantage of the “direct calibration by isotopologues amounts” has to be addressed in the manuscript and the suggestion has to be adapted accordingly. A 0.2‰ in $^{\delta^{13}}$C(CO$_2$) is one order of magnitude above the GAW recommendations$^2$ for which reason the proposed calibration method seems not applicable for instruments applied in the context of GAW. Some of the references used in the manuscript as an example of the alternative “Calibration by delta values” are used in the GAW context with corresponding precision targets. So the context of these references has to be reconsidered.

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

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

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

- Page 7, line 35 and following: IRMSs can also be used to measure absolute abundances of the single isotopologues, but the measurement is in general noisy and very difficult to calibrate. This “absolute” approach has been used in the beginning of mass spectrometry before it has been realized that a relative measurement with IRMS is much more precise than an absolute measurement\(^3\). This is also the case for isotopologue-specific optical systems. The noise in a line ratio is much smaller than the noise of the individual lines because there is a lot of correlated/technical noise on two simultaneously measured lines which cancels out in a ratio (given that the instrument can measure the targeted lines simultaneously in real-time as possible e.g. with a direct absorption spectrometer). It’s not due to the nature of IRMS that the community has converged to go for relative \( \delta \)-scales, but rather due to the more fundamental analytical advantage of measuring relative values with respect to a reference material as opposed to absolute measurements.

**References:**

