

Response to Reviewer 1 on review of “A versatile water vapor generation module for vapor isotope calibration and liquid isotope measurements”

We thank Reviewer 1 for the detailed comments to our manuscript and for taking the time to provide constructive feedback.

We have below responded to the individual comments of the reviewer and indicated how we have improved the manuscript. We have used RED font to indicate our response. We appreciate the reviewer’s comments on improving the figures. In general we have followed all of the suggestions by the reviewer.

Reviewer 1

This manuscript presents a comprehensive and detailed explanation of methods and apparatus that keenly solve some of the formidable challenges that have perplexed field scientists attempting to make and calibrate high quality measurements of water isotopes and water vapor concentration for some time. For those who can successfully implement the technical designs and concepts presented here and apply it to their research, I am convinced it will represent a step change in their ability to make more useful and reliable measurements in a variety of environments. It is clear that this represents a culmination and evolution of concerted efforts, both on the part of the authors, and many whom they cite, in a long term quest to address the challenge of stability in analytical systems of this type. I whole heartedly recommend its acceptance for publication, with some minor edits, mostly technical clarity, and slight improvements to 2 of the figures. If possible, a few photos would really help illuminate the not only the complexity of the system, but it’s likely compact nature and portability.

One of the more important innovations is the advanced PID control of the headspace pressure in the vials by metering between pressurized air and vacuum, leading to remarkable steady metrics in both isotopes and water vapor concentration. An equally head-line worthy finding is the speculation on the effects that cavity temperature control have on the precision of the Picarro instrument. This may not be surprising to some but seeing it here along with all the other metrics is compelling. Not only have the authors achieved in creating a remarkable instrument/inlet system, but they have tested the system thoroughly and produced metrics that quantify and demonstrate its stability in a convincing manner.

Detailed Line by Line:

Line 23: Typo: “... as a calibration system have been document to ...” -> should be “as a calibration system has been documented”.

Corrected.

Line 25: Add “, assuming 1 hour/day for calibration” to the end of the sentence.

Corrected

Line 42: Add parenthesis to the d-excess equation: $d\text{-excess} = dD - (8 \times d18O)$

Corrected

Line 77: The use of a selector valve is mentioned, but is not shown in figure 2.

New schematic in manuscript. Schematic with selector in supplementary material.

Line 180- 190: Mixed past and present tense (was and is).

Corrected

Line 186: An explanation of why a PTFE fitting is used instead of stainless steel would help. PTFE ferrule and nut have been used to not deform the PTFE capillary. Text inserted.

Line 196: The use of the term “oven” is a bit confusing or misleading. Consider using Heated assembly, or perhaps heated tees, or reaction vessels, or? The word oven connotes and enclosure of some kind, which is not really the case?

We here use the term oven to represent both the heating block and the heated tees. We have however specified the text such that it refers to “module is highly scalable in terms of number of heated tee units” instead of oven units.

Line 202: “The water vapor is produced in the oven is routed toward the output of the system....” How? Stainless steel capillary or?. Specify here.

We have updated the text such that it now reads:

...is routed toward the output of the system through the stainless steel valve manifold and a copper tube where the vapor is measured using...

Line 208: Spacing issue in the word “different”.

Line 209: “In a second modification...” Was there a first modification? Perhaps it could just be ‘In a subsequent modification’ or similar.

We will use the term “subsequent” - this refers to the use of a selector valve “multiport selector (C25-3180EUHA, VICI) to inject samples from the different vial holders continuously, without needing to switch the oven” instead of an multi-oven unit.

Line 233: Spacing issue in the word “analyzer”.

Line 275: It is not clear what is meant by “...Suboptimal management of memory effect[s] during Allan Deviation tests.” Is this in the Picarro instrument, or in the inlet system described Here?

We are here referring to the memory effect due to the combination of calibration system, the inlet and Picarro’s cavity. We don’t know if authors of the mentioned studies had let the system to “prime” for 12 hours or so and hence we have introduced the sentence “, such as not priming the system for upto 12 hours using the same standard”.

Line 289: The authors system really deserves a fancy acronym name of some type 😊 as opposed to “the vapor generation module”. Not just for cache, but to more easily distinguish it from the “vaporizer using the autosampler”. Perhaps one could refer to the Picarro vaporizer/autosampler combination, or similar?

Thank you for this suggestion - we have proposed to name it VG Module

Line 291: Consider adding something like: “ The large difference in these values is discussed further in section 4.4 on memory”.

Good idea - corrected.

Line 320-324: This stable region at ~12,500 is a very interesting finding. Any speculation as to what may govern this (?) could be useful.

We believe that it could be the point of “stable equilibrium” between pressure-driven liquid flow rate and the dry air flow of the calibration system?

Line 342: Perhaps also include Rozmiarek et al. (2021). [<https://doi.org/10.5194/amt-14-7045-2021>].

Added

Line 408: “A 1 m length of 3.125 mm OD copper tube”. Maybe explain why such a long length was needed?

The length of the tubing could have been reduced if placed on the same table top. However, the lengths were adjusted to enable connections of the instruments placed over different tables. Clearly to improve the memory effect further one should decrease the length of tubing.

Line 419: Typo “This support[s] the hypothesis...”

Corrected

Line 430: Typo (?) “...in phase coherence between d18O and cavity [?] for periods...” I think you mean cavity temperature and/or pressure?

Correct - we meant cavity temperature

Line 439-441: This is a MAJOR finding that the precision for measurements could be improved by up to a factor of 2 if the PID driven cavity-temperature cycles could be dampened. Might deserve higher placement or highlighting some how. No doubt, manufactures will be very interested in this, along with the many other findings !

Thank you. We further notice that the “bump” is occurring for the same integration time as liquid sample measurements. We have further expanded on this in the abstract and added the following sentence “, which if improved upon could result in an improvement in measurement precision of up to a factor 2.”

Line 493-494: The reader will greatly appreciate the honesty implicit in the statement “We do not have an explanation for why the stainless steel capillary was performing better”!

Thank you. We do try to also highlight that we not always know why it works better.

Line 495: “...we had partly success” should be ‘we had partial success’.

Corrected

Line 496: “As we will discuss in details below[,]” Consider: ‘As we will discuss in detail below[,] the clogging...etc.’

Corrected

Figures and Tables:

Figure 1: This needs some work. While schematically correct (after considerable time discerning this), it could be made far more accessible to the general reader, by including some more details and labels. For example,

- label (or describe in the caption) the type of compressed air (nitrogen, zero air, or?);
- labeling the 3-way metering valves as such (these are key to the design);
- Instead of the part number of the R/H probe, consider putting that information in the text or caption, and simply call it for what it is “Precision R/H probe or similar”.
- How do 4 “ovens” converge into a single outlet?
- Is there a selection valve missing from the diagram?
- Oven unit could use a foot note “See figure 2” in its label
- If AMT allows use of color(s), consider using them to further distinguish flows of air, water and water vapor, with thicker lines. Or use words on the lines.
- Label the 1-4 psi pressure regulator (?) as such.
- Use bigger font were possible
- Not clear what the dashed red lines are, other than T1 and Tn, indicating there could be multiple vials.
- Is the input to MFC 1 really an unregulated line to the compressed gas? I suspect a regulator is in there somewhere (in addition to the 1-4 psi).
- Output could include “open split to analyzer” or such.

Figure 1 edited following reviewer comments.

Figure 2: Drawing of the heated tee sections is good. Some improvements could include:

- Consider adding the word “oven[s]” to the block of heated tees. (I know its in the caption, but will help the reader).
- Consider showing some type of dry air inputs on the left, H₂O on top, and vapor coming out the right side more clearly . Maybe add some capillaries?
- Arrow pointing to PTFE capillary is actually pointing to he Swaglok nut (picky, I know).
- Consider labeling the bottom of the assembly with “2 ml vials with water” or such.

Figure 2 edited following reviewer comments.

Figure 3, 4, 5, 6, 7 & 9: All Good

Figure 8: Cosmetic improvement: Consider smaller fonts.

Tables

Table 1: Good. It may be obvious, but consider spelling out in the caption that BER is Bergen water and SP is South Pole water.

In fact BER is Bermuda water 😊

Updated

Table 2: Good. Need to widen 2nd column a tiny bit to better accommodate heading text. Consider defining RSD either here in the caption or in the text.

Corrected

Table 3: Good.