

Response to Reviewer 5 on review of “A versatile water vapor generation module for vapor isotope calibration and liquid isotope measurements”

We thank Reviewer #5 for valuable inputs, which have improved the readability of the manuscript. As suggested by the reviewer we have placed our results into a broader perspective by comparing our ^{17}O -excess measurement performance with what we believe is the most recent work such as Davidge et al. 2022. We have responded with **red font** below.

The paper reports general improvements in the author's previous device. I found it challenging to understand the manuscript in detail simply because it is not written for broader readers. Too many self-citations (14/43=32%) imply a narrow target readership. It would be preferable to clarify and discuss the position of this study from a broad perspective, as related studies exist. For example, Graaf et al. (Isotope ratio infrared spectroscopy analysis of water samples without memory effects, Rapid Com. Mass, 2021) reported no memory effect for liquid measurement. Although these test results would be helpful for certain people, this manuscript should be thoroughly revised before acceptance.

We agree with the reviewer that the study of Graaf et al. is very interesting, especially the result focused on the reduction in memory effect. The setup of Graaf et al. follows the development of Gkinis et al. 2011, which uses a peristaltic pump to push water into a heated tee. We note that we already reference this development in our introduction. Graaf et al. then injects a sample using an autosampler into a heated chamber designed similar to the Picarro High Throughput vaporizer or the LGR vaporization system. However, the instrumental development of Graaf et al. suffers from the same design issue as the Picarro SDM or Picarro/LGR autosampler/vaporizer in that that it does not allow an unlimited injection of a sample as described in section 2.1 Graf et al. *“This volume serves to spread out the sample peak over a wider time interval, which facilitates precise data integration over the sample peak.”*

We believe that the continuous injection of a sample or a standard such as documented for 92 hours is a key development of our system. The long injection time allows us to quantify the Allan Deviation for integration for more than 24 hours which allow us to detect optimal injection times for obtaining low standard deviation levels. The analysis also allows us to compare the performance of the two systems.

For example: We report an Allan Deviation on ^{17}O -excess on 10 minute averaging time to be around 10 per meg. This value should be compared to the 1-sigma precision on ^{17}O -excess for a single injection presented by Graaf et al which is shown to be 60 per meg.

Graaf et al report a standard error of 10 per meg for ^{17}O -excess:

“In the system presented here, the statistical uncertainty on $\Delta^{17}\text{O}$ can be reduced to the 10 per meg level by determining standard errors of the mean of 20 single injections, which corresponds to 3.5 h analysis time per sample.”

Using similar measurement times, we show that the reproducibility for samples measured 4-5 times (over 3 hours each time) on separate days reveals a standard error of the mean always ≤ 4 per meg. (It is important to note that the precision reported in our manuscript is defined as the standard error of the mean multiplied by the Student's t-factor for a 95% confidence limit, as described in Barkan and Luz (2005).

However, we do note that our study is not the only recent study presenting similar low errors on 17O-excess. We have therefore added the following sentences to place our result in perspective: *Such reproducibility is comparable to precision achieved with IRMS (e.g. Barkan and Luz, 2005; Steig et al., 2014) and to the total error obtained within the latest development in continuous flow analysis of ice cores (Davidge et al., 2022)*

(1) There are many typos. I cannot point out all. Following are the typos found only on page 1.

We agree that this should have been fix by us and we have therefore gone through the manuscript carefully to remove any issues. Hopefully, it is much better now.

L17: show > shows

Fixed

L22: Remove "as" at the end of the sentence.

Fixed

L23: have > has

Fixed

L23: document > documenting (or documented?)

Fixed

L30: falls > fall

Fixed

(2) An example of the limited readability only on Figure 1.

New schematic done following reviewers comments

L.132: "...module is an improved and revised version of an original prototype in 2014..."

> Please briefly explain the previous system. A few sentences will be fine.

Fixed

L. 134: "A four-ovens version was used in this study."

> What is a four-oven version? Why does Figure 1 illustrate only one oven?

We agree that Figure 1 perhaps was not so clear on this point, as Figure 1 illustrated “an oven unit”, which was then further described in Figure 2. We have therefore updated Figure 1 to show the individual ovens as well as provided a more detailed drawing of the oven themselves in Figure 2.

In Fig.1, caption: "... in open-split mode..."

>Please explain the open-split mode.]

We have updated the text so that it now reads “...of the vapor generation module in open-split mode to allow the part of the vapor stream that is not going into the Picarro instrument to escape”

Fig. 1: There are no explanations about abbreviations and lines. Please define or explain "P1", "T1", "Tn", "Vacuum line", "red dotted line", "black dotted line", and "black solid line".

We have prepared a revised version of Fig. 1. All the lines are now color-coded and a legend is included in the figure. Reference to the vials ($T1...Tn$) has been removed. The schematics now include reference to the product number of the valves.

Specifically we have added the following information to the supplementary material and referenced it in the caption of Figure 1:

V1_x are manifold-mounted three way solenoid valves (SMC, VO307-6DZ1-Q, VV307-01-043-01N-F)

V2_x, V3_x, V4_x are manifold-mounted solenoid valves (SMC, VDW23-6W-1-G-Q, VV2DW2-G0401N-F-Q)

Humidity sensor is obtained by combining temperature sensor (Analog Devices, AD22100STZ) and relative humidity (Honeywell, HIH-4000-004).

MFC1 and MFC2 are mass flow controllers for air (Aalborg, model GFC17A)

Dual-valve electronic pressure controller is ALICAT model PCD-5PSIG

Vacuum pump is KNF membrane pump model NMP830KPDC

PID control is achieved by LabVIEW software.

Please add several photos of this system in supplementary information.

We have added figures to the supplementary material under Supplementary Images.