

Interactive comment on “A dedicated robust instrument for water vapor generation at low humidity for use with a laser water isotope analyzer in cold and dry polar regions.” by Christophe Leroy-Dos Santos et al.

Anonymous Referee #2

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1 Overview

The manuscript “*A dedicated robust instrument for water vapour generation at low humidity for use with a laser water isotope analyser in cold and dry polar regions.*” by Christophe Leroy-Dos Santos et al., deals with a very non-trivial challenge in the area of in situ isotopic analysis of water vapour in polar regions using Infra Red Spectroscopy. The very low water concentration levels, typical for the atmospheric air in polar areas and in particular the very dry regions of East Antarctica pose a big challenge

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for the optical spectrometers used for in situ measurements of the isotopic composition of the vapour. One part of the challenge has to do with the very low signal to noise ratio in the measurement that results in a poor analytical precision. The second challenge relates to the observed dependence of the isotopic measurement on the water concentration level of the sample in the optical cavity of the spectrometer. In the more modern versions of these Cavity Ring Down Spectrometers, this dependence is addressed with in-factory corrections that typically take into account changes in the absorption spectrum and can provide high quality measurements down to $[\text{H}_2\text{O}] \approx 2000$ ppmv. Below this level, additional corrections need to be performed usually requiring the generation of a vapour stream with stable values for $[\text{H}_2\text{O}]$ and $\delta^{18}\text{O}$ and δD .

In this work, Santos et al propose a water vapor generator that is able to provide a stream of vapor with stable $[\text{H}_2\text{O}]$ and isotopic composition, using a combination of syringe pumps and an evaporation chamber aided by flow control instruments. This is a paper that belongs to AMT, providing a tool that is important for polar research. While the scientific significance of the work is undoubted, the manuscript lacks clarity to the extent that the scientific quality, even if apparent, is not easy to judge. Additionally, the presentation quality is fair and the manuscript lacks the use of standard nomenclature commonly seen in technical publications of this type in AMT and other instrumentation oriented journals.

Below I comment on some of the major issues I believe the authors need to address and I propose some changes and experiments that in my view are essential for this study. Considering the importance of the problem the manuscript deals with, I would like to see it eventually published in AMT, after the authors proceed with some major revisions. Perhaps it may in fact be easier and more clean if they start fresh with a new submission, though this is something the editor and the authors should decide.

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2 Remarks

2.1 Evaporation Model

The theoretical foundation of the vapor generator presented here is described in section 2.1 of the manuscript. It is based on the assumption that a constant flow of water ending on a syringe needle tip combined with a finely controlled flux of dry air will produce an isotopically stable stream of vapor via a zero fractionation process. A prerequisite for this, is that the size of the droplet remains stable throughout the experiment. It is still a question to me how a droplet that sustains its size by constantly losing mass on its surface (regained by the incoming liquid water flow) via evaporation yields a vapor stream that has the same isotopic composition as the liquid. This is a typical Rayleigh evaporation likely with a strong kinetic component due to the very low humidity of the carrier gas and the quick -but incomplete- removal of water molecules from the droplet. Even though the treatment of the model has been presented in previous works, this is so central to this system that at least an appendix with more information is needed.

2.1.1 Some points to consider

- How is the size of the droplet controlled when there is no camera or some other monitoring tool inside the evaporation chamber?
- The manuscript mentions in Line147 that the fractionation factor by Cappa et al (2003) are used. But why if there is no fractionation?
- The manuscript claims that under steady-state the isotopic composition of the generated vapour does not depend on the injected flux of water nor the specific humidity. Since this is a technical paper I would appreciate a simple experiment where the flux of the carrier gas is ramped up and down allowed to reach steady

Fig. 1. 6-port switching valve - position filling

state. I have a very hard time seeing how this experiment will produce a vapor stream of the same isotopic composition equal to the $\delta^{18}\text{O}$ of the liquid water. Similarly if the specific humidity of the carrier gas is changed one ends up with a simple mixing experiment (Mook , 2000) where the resulting vapour isotopic composition naturally will be different.

- Throughout the whole manuscript, I have not seen a note on the temperature of the evaporation. This is a critical parameter affecting the efficiency of the evaporation, the saturation vapour pressure of the mixture and the fractionation factors in the (Cappa et al , 2003) parameterization. Since there is no active control and regulation of the temperature, all these parameters will vary.

2.2 Presentation–Standard nomenclature

Any physicist or engineer with moderate training in laboratory instrumentation should be able to look into the flow diagram of a manuscript in AMT or any other equivalent journal and get a basic idea of the method described in it. It is a very important element of a publication of this type, therefore it is my view that the authors should use standard P&ID nomenclature. The current flow diagram is a collection of coloured boxes from which little can be understood. Part of the text uses the photograph supplied (Figure 3) to explain the system something that confuses the reader even more.

2.2.1 Points to consider

- There are standard P&I symbols for valves, pumps, gauges etc that should be used, while colour should be added only if it aids in better explaining the system

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and not cosmetically. Standard names for the components should be used. For example three pumps with three different descriptions (pressure pump, pump and picarro pump) are found in the block diagram when they (most likely) are of the very same type ie vaccum pump.

- One of the main elements of the paper according to the authors is the “double 3-way valve” added to the system. The valve’s type is a 6-port switching valve and a standard symbol for it exists that should be used in this manuscript. It is central to describing the cycles of the system. Feel free to use the supplied (arguably not perfect) Fig. 1 that I am including and describes the valve operation for the syringe filling position.
- Flows and pressure set points for the regulators also belong to the P&I diagram and since the authors claim that they are important to the operation of the system should be given. A table with the ID numbers of the control units and their set points would be very much appreciated. Currently Table 1 blends names of components from Figure 2 and Figure 3 so the reader has to guess. This is not informative.

2.3 Experimental System–Explanation of operation

Section 2.2 of the manuscript contains information on the principle of operation. One of the puzzling pieces of information in this section is the carrier gas flow. Following the block diagram and the information in Table 1, we see that for the “Drying Mode”, the Flow Controllers A and B sustain each a 400 sccm^{-1} flow through the system. The block diagram does not indicate any open splits and for this particular mode the inlet valve is closed and the exhaust vacuum pump is disabled. This is an immense flow for the standard of a picarro spectrometer that normally can sustain its cavity pressure with sample flows in the order of $30\text{-}100 \text{ sccm}^{-1}$.

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Similarly, during the injection of Standard A or Standard B, the flow is in the order of 450 sccm^{-1} , a very high flow level. In this mode though the exhaust vacuum pump is enabled, however we see that the lines of Standard A and Standard B are connected. Thus in Standard A mode, valve B is closed and the generated vapour from standard B, hopefully is evacuated via the exhaust vacuum pump. Is the pressure of 905 mbar enough to make sure that all the 150 sccm^{-1} of standard B are off the system and not mixed with the vapour from Standard A? Why was this value chosen and what kind of tests assure that the two lines are never mixed even though physically connected. The safe way to proceed here would be to simply isolate the two channels, remove the pressure regulator and the vacuum pump and simply install two 3-way valves in the position of valves A and B (which I assume are On/Off???) on which one port goes to the instrument inlet and the other is simply open to the atmosphere in an open split configuration.

2.3.1 Points to consider

- A more thorough description of the flow path is needed and the issue of possible cross contamination between Standard A and B should be addressed.
- The flows are very high - How does the picarro cope with this condition?
- There is no information on the volume of the evaporation chambers and no mention regarding the temperature of the system.
- There are references to a two standard calibration protocol in this section. It is not exactly clear if this concerns some water concentration correction calibration or a linear slope SMOW-SLAP calibration—see specific comment on the notable absence of any reference to SMOW-SLAP below.
- I assume that the system is also used in order to perform a SMOW-SLAP calibration. How are evaporation/fractionation effects in the standards' vials handled?

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Based on Figure 3 we see no precautions concerning this.

2.4 Evaluation–Measurement Stability and precision

The manuscript lacks important information on the evaluation of the performance of the system. Section 3.1 assures the reader that no fractionation is observed during the generation of the vapour and its transfer in the flow lines while the agreement with the commercial standard delivery module is within 0.2 and 1‰ for $\delta^{18}\text{O}$ and δD respectively. It is almost impossible to judge these discrepancies based on figure 5 and in fact when looking closely it is rather difficult to see how the differences between the two systems are of this order.

With respect to figure 4 and the evaluation of the precision for $[\text{H}_2\text{O}]$ and $\delta^{18}\text{O}/\delta\text{D}$ I strongly believe that the manuscript should include a proper Allan variance test (Werle et al , 2011; Steig et al , 2014). It is obvious that the system experiences drifts, whose origin is the vapour generator. Calculating the standard deviation on a 10 min window of a time series that obviously has a changing mean value looks and feels like possible cherry-picking.

2.4.1 Points to consider–Suggestions

- Show better evidence of zero fractionation. If you choose the SDM as a measure of comparison show a detailed comparison and plot the results clearly. The axes of fig 5 span 300 ‰ for δD . It is impossible to say anything.
- Calculate the Allan variance of the system for 4-5 $[\text{H}_2\text{O}]$ levels. Let one water run for several hours and so you get a more honest idea about precision and drifts for all three parameters under consideration. It is a very simple experiment that can provide a valuable insight and by looking in the bibliography it is a rather standard evaluation tool for laser spectroscopy based measurements.

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2.5 Water concentration correction

The water concentration correction is described in section 3.3 with Figure 5 being the main source of information for this part of the analysis. I would consider this one of the most important sections in the paper and unfortunately it spans only one paragraph. It is repeated in the manuscript that the system presented here is superior to the commercial standard delivery module below the level of 500 ppm. How can we see this when the SDM measurements in this are of $[\text{H}_2\text{O}]$ are not presented (measurements stop at $[\text{H}_2\text{O}] \approx 2000$ ppm)?

The dataset in Figure 5 presents the difference of the raw isotopic value and a value that the authors call “reference” and “real”. These words commonly refer to very specific things in isotope geochemistry and my guess is that the reference value is a SMOW-SLAP calibrated value (?). The term SMOW-SLAP calibration is not to be found at all in the manuscript. It is to some extent problematic that a water concentration correction measurement compares a raw value at a number of $[\text{H}_2\text{O}]$ levels with a value post SMOW-SLAP calibration. Please see my comments on SMOW-SLAP in the next section.

The type of correction is not described in the manuscript. This is what this work is all about. There can be various approaches on how it can be done (see for example (Schmidt et al , 2010; Gkinis et al , 2010; Aemisegger et al , 2012)) but the authors need to be open and specific about what they did exactly. Moreover (Schmidt et al , 2010) suggest that the response to changing $[\text{H}_2\text{O}]$ levels varies with the isotopic composition. I do not know how important this effect is for this present work, but I believe that the authors should perform two separate experiments with two different waters (technically the system offers this possibility). It would also strengthen their claims for a vary stable system if they show the full experiment with its raw data as a function of time and not only the averages.

There is also a claim in this section that the stability of the system allows via the

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daily measurement of standards waters to quantify instrumental drifts. There is no strict evaluation of the stability of the system so far and I think that a proper Allan variance test at various levels of $[\text{H}_2\text{O}]$ is necessary. But even in the absence of an Allan variance test the data given in Table 2 do not necessarily indicate instrumental drifts. All the isotope data in the table are within $1 - \sigma$ of the noise level for a 10-min period mentioned in the caption and there does not seem to be a one way trend. So how is it possible to say anything about instrumental drifts? Also the noise levels mentioned in the caption of Table 2 are very different for roughly the same $[\text{H}_2\text{O}]$ when one looks at the data of Figure 4 (4.5 versus 14).

2.5.1 Points to consider-Suggestions

- A clear description of the correction is missing. Some math is needed here.
- An experiment at two different isotopic levels showing the raw data versus time will show if there is an isotope effect in the water concentration dependence.
- A proper quantification of instrumental drifts (and this concerns the system as a whole and not only the spectrometer) can be done with a proper Allan variance test.

2.6 Lack of reference to SMOW-SLAP calibration

The main goal of building a water vapour generator as a peripheral for isotope measurements of water vapour is to be able to calibrate the dataset on the SMOW-SLAP scale. This is the only way to communicate and compare the measurements with other existing data sets and produce some science out of them. It is also even more important if the deuterium excess parameter will be studied as it is very sensitive to this calibration procedure. Therefore it appears very awkward that a manuscript dealing

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with this topic does not include a single note, comment or reference to this very important step Of the measurement process. The dataset presented later in section 4 of the manuscript are impossible to evaluate if they are not calibrated in the SMOW-SLAP scale.

One more purpose of performing such calibrations, is that they can reveal possible accuracy issues in the instrumentation system. Given two standard waters one should be able to produce a calibration line and thereafter measure a third water of known isotopic composition treating it as an unknown. If the resulting value lies beyond the $3 - \sigma$ range then there is likely something wrong with the system. That could be any part from the water standard storage to the water vapour generation system or the spectrometer itself. Currently there is no way to say anything about the accuracy of the system. With this in mind, section 4 of the manuscript is of very little use as the dataset is reported on some local instrument scale.

A SMOW-SLAP calibration experiment at various $[H_2O]$ levels using the SDM and the current system would provide a proper comparison between the two systems and therefore it would be a very important addition to the manuscript.

2.6.1 Points to consider

- A proper treatment of the SMOW-SLAP calibration step is notably missing.
- Performing 2-standard calibrations and measuring a third water standard treated as an unknown will be a valuable -almost essential- addition to the manuscript, offering important information on the accuracy of the system.
- Since a lot has been written about the performance of the commercial SDM it will be proper to perform 2-standard calibrations for various $[H_2O]$ levels and compare the results.

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2.7 Conclusion

I encourage the authors to revisit the manuscript and take the necessary steps as their contribution with this experimental system could be important for the community. The manuscript is to some extent rushed and some important aspects of the evaluation of the system are either missing or non-standard practices are followed. Some of the points I am raising here, are not only personal opinions but also guidelines of the International Atomic Energy Agency. I am confident that the authors can perform the necessary measurements/experiments and revise the manuscript.

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