Review of "A flexible device to produce a gas stream with precisely controlled water vapour mixing ratio and isotope composition based on microdrop dispensing technology"

This paper presents a new device based on two microdrop dispenser heads that allows to inject a controlled amount of water with known isotopic composition into a heated evaporation chamber flushed by a dry carrier gas for subsequent analysis with a laser spectrometer. The authors argue that the novelty of this device is its flexibility in terms of producing air samples with a range of different water vapour mixing ratios and isotope compositions varying between the two end-members of the liquid water samples feeding the two dispenser heads. The authors show two applications of the new device: 1) the detailed characterisation of the well-known water vapour mixing ratio dependence of isotope measurements with laser spectrometers and 2) the production of a stable background water isotope signal for the precise measurement of microfluid inclusions in stalagmites.

The paper is interesting and well-illustrated. The major innovation is the combination of two dispenser heads instead of one, which gives more flexibility in the generation of water vapour samples with a range of different isotope compositions and water vapour concentrations. While most of the text is well-written and easy to follow, there are a few parts that are written in a misleading way, where I suggest that the reader guidance and accuracy of the description could be improved (see my minor comments below).

The paper should be published in AMT after the following two major points and a longer list of minor comments as well as a few technical aspects have been addressed:

M1: Given that the key innovation of the proposed system is based on the combination of two dispenser heads for being able to produce a series of gas streams that cover a range of different water vapour mixing ratios and isotope compositions, a solid assessment of the uncertainty of the predicted reference properties ($[H_2O]$, δ^2H, $\delta^{18}O$) should be provided. Currently, this aspect is very difficult to assess. From Fig. 8 it seems that the RMSE of the obtained mixtures of standards is very large and therefore the system's characteristic uncertainty in the reference isotope composition and mixing ratio when using the two dispenser heads simultaneously seems to me an important issue.

M2: I am not convinced that the relatively complex water vapour mixing ratio – isotope dependency correction is really needed in the second application for micro fluid inclusions in stalagmites, because the water vapour mixing ratio of the background airstream is well above 10'000 ppmv and the variations due to the microfluid injection peak is in a range of values where this correction is not usually needed. Could the authors show the impact of this correction on their aliquot of a natural carbonate and/or their samples used to mimic real fluid inclusions? It's a major point because the authors argue that this is an important additional processing step that was neglected in the previous literature (L. 430-437).

Minor comments:

1) L. 1, L. 22 and at other places: "a flow of **air-vapour** mixture" is a bit confusing: not clear what vapour of which gas and air does a priori comprehend water vapour as well. The terminology used in the title seems more precise to me: "a gas stream of a pre-determined water vapour mixing ratio and isotope composition".

2) L. 6: "water vapour mixing ratio", just mixing ratio can be any gas or isotope.

3) Abstract: the abstract is a bit short and lacks key information on the new device. It would be more informative to add a few key numbers in the abstract such as the range of flow rates tested, explain what limits the flow rates in the device (key for more recent fast-response CRDS instruments operated at high flow rates). The range of water vapour mixing ratios and isotope delta values tested as well as the quality of the delivered calibration or background gas stream could be mentioned (precision, stability).

4) L. 15: I think Graf et al. 2019 is a nice example for subcloud processes involved during precipitation but not weather systems in general. Thurnherr et al. 2020 cover a broad range of latitudes and different types of weather systems, which would be a better fit here.

5) L. 16: "analyser properties" is a bit unspecific, be more precise.

6) L. 17: "the variability of the calibration system", what does that mean?

7) L. 15-19: Total uncertainty resulting from a variety of instrument characteristics at different water vapour mixing ratios and the characteristics of inlet systems were tested extensively in the two early publications Sturm and Knohl, 2010; and Aemisegger et al. 2012. Application in the field with aircraft-based measurements (Sodemann et al. 2017) and for near-surface humidity gradients (Seidl et al. 2023) were carried out in the more recent ones. This is a bit misleadingly written and should become clearer from this section of the text.

8) L. 29ff: I am not convinced that the microdrop system that is proposed in this paper alleviates all the mentioned problems: given the small liquid reservoir, the isotope composition of the standard liquid in the glass vials should be monitored as well for a reliable normalisation to the VSMOW-SLAP scale. What would be more convincing to me at this stage is to mention primarily that in the bubbler system the reference isotope composition of the vapour phase has to be predicted from equilibrium fractionation, which requires precise temperature regulation of the liquid phase in the bubbler. This problem is overcome in other devices by complete evaporation. Monitoring the liquid isotope composition is a must also in systems with complete evaporation including an SDM standard bag. When using large water reservoirs of several litres the close-up monitoring of the liquid is not so essential in bubblers because the changes are much smaller than the precision of the reference measurement with IRMS or laser spectrometry.

9) L. 50-51: "limited possibility to regulate the mixing ratio of the water vapour in the airflow", which is not really needed for the mentioned application.

10) L. 64-65: The mention of flow rates in between the water vapour mixing ratio range and the different isotope composition is disturbing the logical flow of information in

the reader's mind: Maybe something like the following would help: "… that provides the combination of a precise stream of water vapour across a range of water vapour mixing ratios and isotope compositions as well as operation at various flow rates between 50 and 250 sccm." -> group the range of mixing ratios and isotope compositions together, flow rates is a different aspect also from an operational perspective.

11) L. 71: "and as a component in specific laboratory applications" this is a bit unspecific. Please be more concrete.

12) L. 73: Here it would be very nice to be more precise about the gas stream of a preset background humidity and isotope composition for fluid inclusion analysis. A reader who is unfamiliar with this technique is lost here (see also my minor comment 53).

13) L. 75-89: This paragraph is very dense with information and a bit difficult to follow. The first sentence starts with introducing the advantage of the microdrop generator in covering "a wider range of applications with CRDS analysers" than with currently available devices. But there are a countable number of applications, and the currently available devices are optimised for the tasks at hand. I rather think the advantage of the microdrop generator is the flexibility of it to produce a wide range of (predetermined) water vapour mixing ratios and isotope compositions. The application to microfluid inclusions in stalagmites is nice but this high flexibility is actually not needed there.

14) L. 77: Why are the authors so strict about the water vapour mixing ratio uncertainty? Is this useful in one of their applications? I thought they target the isotope composition of different vapour/liquid/fluid inclusion samples and not the absolute water concentration.

15) L. 81: I believe the first publications with fast-response analysers with flow rates above 100 sccm are Thurnherr et al. 2020 ACP with a detailed assessment of the impact of the flow rate on the water vapour mixing ratio dependence on isotope measurements in their supplement and Bailey et al. 2023 ESSD. From these publications with flow rates of about 300 sccm through the cavity it becomes clear that flow rate limitations of calibration systems is an important challenge.

16) L. 82: This sentence should be removed or moved to the discussion in the conclusions (see also my minor comment 74), the response times of the inlet is not tested in this publication and cannot be tested with the proposed microdrop dispenser because the flow rates are much too small (would need several liters per min to be of interest for this sort of application).

17) L. 88: The requirement of being field compatible seems ambitious and I don't fully understand it. How well do the dispenser heads work in very cold environments with vibrations and at low pressure? In principle drift correction in the field could be done with simpler existing systems, the advantage of this system resides in the possibility to characterise the water vapour mixing ratio – isotope ratio dependency in detail. This is more a laboratory than a field application.

18) L. 92: SDMs can go well below 6000 ppmv.

19) L. 94: What does "Injections with the autosampler are feasible with a specific method" mean?

20) L. 95: This joins my major comment M1: unless you are able to very precisely predict the isotope composition of your mixture with the two dispenser heads you cannot really overcome this limitation from other systems.

21) L. 101: this doesn't become clear from the schematic in Fig. 1.

22) L. 103: this is a very small amount of water which can be rapidly impacted by evaporative enrichment in the field!

23) L. 106: "retention time of water vapour" are interactions with the chamber walls meant here? If yes, to me "memory effect" would be clearer.

24) L. 140: how robust are the voltage and frequency settings and their associated efficiency to prolonged usage?

25) L. 148: "We can used this relation between drop size and mixing ratio to compute the effective drop size…" I am a bit lost here. Do you mean the relation between the frequency and the mixing ratio can be used to estimate the effective drop size?

26) L. 154 and Fig. 3: is it only my print out that make the curves in Fig. 3 not look linear?

27) Fig. 3b: Why is the H2O mixing ratio coverage worse with the settings for panel b than in panel a?

28) L. 161: This seems to be key, indeed. Can the uncertainty from this fitting procedure be quantified in ppmv for a series of runs? And how frequently does this readjustment of dispensing parameters need to be done?

29) Fig. 4: I am not sure that I really understand the meaning of this figure. What does all dispersion parameters mean? Could this Figure be placed a bit more logically in the discussion. A part from a useful diagnostic, I don't see the use of it? Is it possible that only showing the blue and red distribution would help the reader because these are the selected settings. In general, I am not sure that the reader is interested in the full distribution with all your tested dispersion parameter setting.

30) L. 192: here and elsewhere: it is "Allan" variance not "Allen" and the adequate reference would be Allan, 1966 Allan, D. W.: Statistics of atomic frequency standards, Proc. IEEE, 54, 221–230, doi:10.1109/PROC.1966.4634, 1966.

31) Eq. 1: I think the authors mean $y_{i+1}(\tau)$ not $y_i+1(\tau)$.

32) L. 206: The SDM is optimised for the precision of the δ^{18}O and δ^2H not for the mixing ratio. For a fair comparison with a high quality mixing ratio signal, a dew point generator should be used.

33) L. 225: this is understandable only if the basic concept of fluid inclusion peak measurements on a stable background has been explained in the intro. Maybe a reference to Section 7 could also be added here.

34) L. 254: "The linearity of this mixing is provided over a range of mixing ratios". I can't really evaluate this statement based on Fig. 8a. How about coloring the data points with the mixing ratio?

35) L. 255: "At lower humidity than 5000 ppmv deviations from the linear mixing become apparent" Also here, I can't really see this in Fig. 8b, which shows the RMSE of δ^{18}O and δ^2H from the observed mixing line at different water vapour mixing ratios. The RMSE is by the way very large implying that the predicted reference isotope

composition of the gas stream has a large uncertainty making it very difficult to me to effectively these mixed samples as reference calibration samples.

36) L. 260: what is Mix000 and Mix 100? This is the first time these labels appear.

37) L. 260: Where can I see this bending down (please add a reference to the figure that is meant here).

38) L. 263: the phase space you are showing in Sec. 6 is the correction function in the ln(mixing ratio) vs. δ^2H (or δ^{18}O) phase space.

39) L. 265: the microdrop vapour generator was already connected to the analyser for all the evaluations presented in the previous section. Here you switch from characterising the microdrop vapour generator to using it to characterise CRDS analysers in their water vapour mixing ratio and isotope composition dependency.

40) L. 267: The water vapour mixing ratio and isotope composition dependency is of spectroscopic origin and due to uncertainties associated with the baseline. Even if a system is optimised for measurements at lower humidity levels than 20'000 ppmv this problem occurs.

41) L. 273: This is misleading. The spectroscopic origin of the concentration dependency has been mentioned already in early laser spectrometric instrument evaluation work such as from Sturm and Knohl, 2010 and Iannone et al. 2009.

42) L. 274: matrix gas -> carrier gas

43) L. 296-308: This is very difficult to follow, could the respective sequences be clearly indicated in Fig. 9? This paragraph should be in stronger dialogue with what we see in Fig. 9 for the reader to be able to follow.

44) L. 313: Here I got lost, where do I have to look above or below?

45) L. 315: Can the authors be more precise about the number of outliers they filtered out? This is an important quality measure for the microdrop generator. Because an ideal calibration system needs as little instrument measurement time as possible so minimising the occurrence of "outliers" is a key aim when designing a robust calibration system.

46) L. 320: What is the share of new data points from the microdrop generator vs. the data points from Weng et al. (2020) in this analysis shown in Fig. 10? Could the data points from the microdrop generator be highlighted in a different color or shape?

47) L. 331: the delta value is specified und used in equations 2 and 3.

48) L. 336: this final step was a bit obscure to me. I thought that the correction function is 0 per definition at the reference mixing ratio level?

49) Table 3: the RMSE is most likely very dependent on the mixing ratio? Maybe a Figure showing this dependence as a function of mixing ratio would be more informative.

50) L. 350-355: this paragraph was again not clear to me. Which subsample of available measurements?

51) Fig. 11: The vertical axis is not the raw but the reference δ^2H and δ^{18}O, right? There are no dashed grey lines (at least not in my print out) and what are the blue lines? Would this figure be better readable if it was shown in this format in the appendix (to illustrate the limited concentration effects at high water vapour mixing ratios) and with

a zoom in to 0-5000 ppmv (which is the interesting part) in the paper? Right now one does not see much about the important effects at low water vapour mixing ratios.

52) L. 357: "a constant vapour stream" with known water vapour mixing ratio and isotope composition (very important!)

53) L. 357-366: This information should already be provided in the introduction.

54) L. 369: "memory effects can be removed entirely" is misleading and a bit optimistic. Isn't the advantage of the CRDS technique mainly the ability to measure δ^2H and δ^{18}O (possibly even d17O) quasi-simultaneously with much reduced sample preparation effort?

55) L. 372: "higher throughput and better reproducibility" than what?

56) L. 384: Fig. A2 -> Fig. 12?

57) L. 387-393: connect this paragraph better to Fig. 13, they should be in better text-illustration dialogue to help the reader follow.

58) L. 395: As mentioned in M2 I wonder about the necessity of this step given the high mixing ratio of the background air stream.

59) L. 397: "Mixing ratio -isotope ratio corrections..." this has already been mentioned in point i) just above and appears as an unnecessary repetition here.

60) L. 399: what is meant by "size-δ" relationship?

61) L. 405-414: I got lost in this paragraph. As the authors write at L. 410 this appears redundant. Fig. A1 is not very convincing in showing a consistent dependency of the isotope signals on the injected amount.

62) Fig. A1: To which mixing ratio levels do these injection volumes correspond?

63) L. 407: "drift in values", what do you mean by values?

64) L. 412: the last sentence of this paragraph "Finally,..." is particularly obscure to me. Could the authors illustrate this with a figure?

65) L. 431: Here I am a bit puzzled: the authors write that water vapour mixing ratio – isotope dependency corrections are necessary below 5000-10'000 ppmv (L. 270). But the background gas stream can be designed in such a way that the mixing ratio is larger than this and ideally even close to the optimal water vapour mixing ratio operation level of 20'000 ppmv? So why does this correction matter? Can the authors show how different the isotope signal estimates get when applying vs. when not applying the water vapour mixing ratio correction for their aliquot or the samples used to mimic real fluid inclusions? This is also my major point M2.

66) L. 432: "more correct" than what?

67) L. 434: Why is the precision of the water vapour mixing ratio mentioned here? Isn't what matters for precise fluid inclusion measurements the precision of the isotope signals?

68) L. 455: for which application would horizontally mounted DHs be an interesting option?

69) L. 462: Flow rates between 300 and 600 sccm through the cavity are now used in different applications (aircraft-based and flux measurements) and present many

advantages (e.g. faster response times, better signal to noise ratio at shorter averaging times) but this range of flow rates cannot be covered the microdrop dispenser system. Why is that so, and is an extension to these higher flow rates possible with the given operational range of dispenser head triggering frequency?

70) L. 475: remind the reader that the Picarro SDM is the commercially available benchmark used for characterisation of the microdrop dispenser.

71) L. 475: In the long-term precision (relevant for calibration) the microdrop dispenser is not better than the SDM for the isotope signals (which we are interested in). The dispenser is better than the SDM for water vapour mixing ratio, for which however a dew point generator is needed anyway for precise calibration. Together with the many small problems that occur with air bubbles in the dispenser head, the small amount of liquid that needs to be exchanged regularly, this questions the utility of this system for regular field calibrations. It is very useful for an in-depth characterisation of the water vapour mixing ratio – isotope signal dependency in the lab but apparently not so much for prolonged measurements in the field.

72) L. 477: I don't understand what this sentence implies scientifically. Which specifications are meant here? The dispenser head and mass flow controller specifications or the objectives set by the authors for the system in Section 2? Maybe a reference to section 2 could be added here.

73) L. 495: Could this simply be a numbered list of implications? It would be easier to read.

74) L. 502: Here is the place where the sentence from L. 82 could be brought in: larger flow rates are needed to test the inlet system and the overall response time of different water vapour isotope measurement field setups.

75) L. 502: Again this is misleading, response times of laser spectrometric water vapour isotope measurements were not the topic of this publication. If one just reads the conclusions, this sounds like a result from this study. References to the studies Sturm and Knohl, 2010 AMT (tested Synflex tubings in the lab) and Tremoy et al. 2014 JGR (tested Synflex tubings in the field) should be made.

Technical points:

1) L. 17: **.** Currently
2) L. 67: technology, **which** allows
3) L. 75: "water" vapour
4) L. 76-80: Grammatically and for keeping the reader's attention having (ii) in the same sentence as (i) would be much more convenient.
5) L. 103-104: "one 12 ml glass vial that holds a liquid water standard and which is mounted next to …". It is not the evaporation chamber that holds the liquid water standard, right?
6) L. 161: demonstrates
7) L. 161: "… ~~a~~ suitable dispensing parameters"
8) L. 214: microdrop
9) Caption Fig. 4: dispening -> dispersion
10) L. 348: og -> of

11) L. 369: CDRS -> CRDS
12) L. 464: viscousity
13) L. 509: performed
14) P. 27, Fig. A1: is "assigned" really the term you want to use here on the y-axis? To me this seems to be the "reference".