

Interactive comment on “Water vapor $\delta^2\text{H}$ and $\delta^{18}\text{O}$ measurements using off-axis integrated cavity output spectroscopy” by P. Sturm and A. Knohl

Anonymous Referee #1

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General:

This paper by Sturm and Knohl evaluates the performance of a laser absorption technique (ICOS, Integrated Cavity Output Spectroscopy) for assessing the stable isotope variation in air-H₂O. The instrument is a commercial system from LGR Inc. ('WVIA') and is available since 2 years. The same instrument has already been evaluated in 2008 by Lis and Wassenaar (Anal. Chem. 80, 287 (2008), with the difference that the Lis paper reports on tests using a configuration with an injection port / water evaporator. The Sturm and Knohl manuscript concentrates on a self-made inlet system for standardization involving a piezoelectric droplet generator as employed in ink-jet printer heads and similar to the device described by Iannone et al in J.Atm.Ocean.Tech, 2009. The standardization of water is the critical issue, mainly owing its surface adhe-

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sion, which prohibits the availability of water-in-air standard gases. The piezoelectric droplets allow a complete evaporation of small water amounts inside a bath gas (dry air) with a chance for standardizing a routine measurement system with little fractionation. The paper by Sturm and Knohl covers a lot of experiments for assessing linearity, optimal precision, temperature sensitivity and, last but not least, routine standardization in a comprehensive form.

Questions and specific issues in the manuscript:

1. page 2063, lines 21/22: The best 18O measurements using equilibration and mass spectrometry is 0.024 ‰ see Frew et al, MAr.Chem. 1995 2. p2066, l10-13: Is it really surprising that the non-linearity is the same irrespective of the isotopic composition? Everything else would be a surprise (and disaster). What really matters is that the span between two water reference materials remains more or less constant and that two sufficiently distant standards can be used for scaling the observable range. This is done in the paper using 5 water standards, but the link to the VSMOW/SLAP scale should be made more direct. (I understand that proper calibration was done using the mass spec, which analyzed your 5 standards. In the complete error budget, this calibration will persist, but the accuracy of your technique is good enough to make a direct calibration using the international water reference materials as well). 3. p2066, l19-23: The contamination should be investigated. If the reference material can have such a deleterious effect, real life samples, e.g. from your growth chambers, could cause similar trouble. When the ring down time decreases, this can only relate to an additional, foreign absorber inside the cavity or on the mirrors. If, for instance, organic material interacts with the (hydrophobic) filter used for protecting the cavity from fine dust, it could preferentially absorb an organic contaminant which then would come off very slowly over long periods of time. The only way to avoid such an effect would be to use completely clean air, or to include an on-line oxidation before the filter. 4. p2067, l13. The relatively disappointing 18O precision (0.25 ‰ instead of <0.1 ‰ as would seem possible from the Allan variance) could be related to the coarse temperature

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control of $\pm 0.25^\circ$? 5. p2069, l14-16: As mentioned above, the use of 5 standards is fine and justified (probably too many, though) However, there should be a direct link added for tracing results to the VSMOW/SLAP scale with a traceability chain that is as short as possible. Is anything prohibiting the direct use of VSMOW and SLAP on this instrument? 6. p2076, fig.1: The dripping device is a bit schematic. Do the drops really hit the opposite surface before complete evaporation? Since this is the heart of the technical innovation, a closer look and focus to this detail would be nice. 7. p2082, fig.7: I assume these are the raw instrument data? Or are these fully corrected, including instrument span? In the latter case, this might be a more serious issue, in the former, the temperature sensitivity just calls for a standardization cycle which is short in comparison with the possible temperature change.

Technical issues:

page 2063, line 17: replace 'The one second standard...' by 'The one-second standard'
p2072, l24: replace '...spectrometry and a case...' with '...spectrometry; a case...'

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