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Atmospheric
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Discussions

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

Anonymous Referee #2

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The manuscript titled “water vapor d18O and d2H measurements using off-axis integrated cavity output spectroscopy” by Sturm and Knohl describes the effort by the authors to characterize the performance of the commercial Los Gatos Research Inc. water vapor isotope ratio spectrometer.

In order to produce the water vapor samples of known isotopic composition, they use the technique introduced by Iannone et al. (Geophys. Res. Abs. 9 (2007) 02398 and J. Atm. Oc. Techn. 26 (2009) 1275), which relies on the use of a commercial, inkjet nozzle technology, droplet generator to inject water droplets into a dry-air flow. This technique avoids isotope fractionation by complete evaporation of the water droplets. Whereas Iannone et al. developed the technique to produce very dry air flows for the calibration of an airborne spectrometer (< 5000 ppmv), the current applications asks for much higher water mixing ratios (in fact, the precision of the analyzer deteriorates dramatically below 5000 ppmv). The use of the droplet generator sets this paper apart from the one by Wang et al. (RCMS 23 (2009) 530), who also used the LGR analyzer to measure water vapor isotope ratios, as the latter used a commercial dew point generator for calibration purposes, with its associated Rayleigh-like isotope fractionation.

The paper demonstrates clearly that regular and continued calibration of the analyzer is absolutely essential if one wishes to obtain reliable results. The paper is a bit weak on providing satisfactory explanations for the observed deviations from ideal behavior. However, if proven practical, the proposed set-up and calibration procedure will be highly valuable for water vapor isotope ratio measurements in both ecology and atmospheric research, and therefore of interest to the AMT readership.

Specific questions and comments:

1) P.2057, L. 8-14: The dedicated research instruments to measure water vapor isotopes that should be mentioned here are: Griffith et al., Isotop. Env. Health Stud., 42 (2006) 9; Kerstel et al., Appl. Phys. B 85 (2006) 397; Iannone et al., Isotop. Env. Health Stud., 10 August 2009; and Sayres et al., Rev. Sci. Instr. 80 (2009) 044102.

2) P. 2057, L. 15: A reference to the paper by Wang et al. 2009 could already be made here. In fact, the authors could point out the differences between their own work and the LGR-analyzer calibration effort published by Wang and co.

3) P. 2058, L. 1: As it appears here, the reader may be mislead to believe that the inkjet technology was developed by Iannone et al., which is not the case. They merely used the same commercial device as used in this study. This potential misreading can be avoided by writing, e.g.: " ... jet technology, similar to the system reported by Iannone et al. (2007, 2009)".

4) P. 2059, L. 2: Is the pressure controller part of the LGR analyzer or a custom addition?

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5) P.2059, L. 15 and 19-20: You are not measuring HO2 (the hydroperoxyl radical) but water. Please correct the isotopologue information.

6) P.2059, L.21: This is only part of the definition of the delta-scale. The missing part is that the d2H and d18O scales are fixed to the consensus values for *two* international standard materials: VSMOW(2) and SLAP (Standard Light Antarctic Precipitation). In general therefore, a scale (span) contraction / expansion is required, in addition to the referencing to VSMOW(2).

7) P.2059, L.23: the mixing ratios are presumably by volume. If so, please specify ppmv instead of ppm throughout the paper.

8) P.2061, L.13-25: How does one switch between the different water standards? I imagine that the tubing between the 12 mL vial and the nozzle has a small volume, but that this volume is still large compared to the pL droplet size. It would take some (long) time to use up this amount of water in regular operation. How is the residual water replaced by new water while avoiding serious memory effects? How long does this procedure take, and does the droplet generator restart without additional user interference? It seems that the change-over from one standard water to another is quite cumbersome and may prevent the wide-spread use of the system for repeated calibration with multiple standards (a minimum of two are needed for the span correction mentioned in comment no. 6).

9) P.2063, L.15: Apart from the expected drift behavior at longer averaging times (> 400 sec), both the d2H and d18H Allan plots show a change-over from one white noise curve to a another (higher) white noise curve around an averaging time of ~10 s. What is the cause this behavior? A plausible explanation appears to be that the intrinsic instrument stability of several 10s of seconds is reached, but that further reduction of the Allan variance is produced by (temperature and pressure) corrections to the raw data inside the control software of the analyzer (beyond the control of the operator).

10) P.2065, L. 18: Very similar results to yours were reported by Iannone et al. (Isotop.

Env. Health Stud. 2009), if the difference in water vapor mixing ratio range is taken into account. They observe an essentially zero deviation for d18O, but also a sizeable negative deviation for deuterium at mixing ratios below 1400 ppmv. They point to residual baseline structure affecting the fit of the weak deuterium line.

11) P.2065, L.10: To me it is not surprising that the calibration curves are qualitatively the same. But with sufficient depletion of the deuterium atom, a change in isotopic composition mimics a change in concentration. In fact, Iannone et al. give a quantitative expression (their Eq. 3) that takes this effect into account.

12) P.2066, L.21: The calibration curve changing over time is of course very worrisome. How can you be certain that the change is uniquely related to the change in ring down time? Also, your experience with the supposedly contaminated air tank is highly suggestive of a changing mirror reflectivity, but alignment changes are not rigorously ruled out. More importantly, did you confirm that the calibration curve returned to its original shape when the initial ring down time was recovered? How much variation does the calibration curve show over time spans of weeks or months, and how much does this contribute to the overall error budget?

13) P.2071, L.23: Definitions of “long-term” being highly variable, I suggest to mention instead that these precision numbers are obtained as the standard deviations of one 12-day measurement series.

14) P.2071, L.24: The accuracy of the spectrometer being much more important to the average reader than its precision, I am sorely missing a discussion of the overall error budget. E.g., the estimated uncertainties in the amount correction (0.47 and 0.27 per mil for d2H and d18O, resp.) are already larger than the 12-day precision numbers. Furthermore, the temperature corrections, with their intrinsic uncertainty, will also add to the overall uncertainty. The WVIA against IRMS calibration curves have their own associated uncertainties in both slope and intercept (which should include the uncertainties in the IRMS measurements, and thus eventually also those of the

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international standard materials, which themselves are too precious to be used on a day-to-day basis), which add significantly to the overall error budget. In fact, these calibration curves show substantial offsets with large error bars (-5.8 +/- 1.5 and -2.9 +/- 0.3 per mil for the d2H and d18O offsets, resp.) that should be commented upon. E.g., how stable (reproducible) are these offsets over longer times?

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 2055, 2009.