

Interactive comment on “Calibrated high-precision $^{17}\text{O}_{\text{excess}}$ measurements using laser-current tuned cavity ring-down spectroscopy” by E. J. Steig et al.

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The manuscript reports on modifications made to a commercial, laser-based, liquid water isotope analyzer and its subsequent characterization. The instrument achieves very impressive results that are equal to or surpass those of state-of-the-art mass spectrometric techniques in terms of precision and accuracy for all three water isotope ratios and the derived quantities of deuterium- and ^{17}O -excess (d-xs and ^{17}O -xs). It greatly improves on those conventional techniques in terms of measurement time (sample throughput) and ease of use. It also appears to deliver results comparable to those recently described by Berman et al. (2013) for another optical instrument, and it promises a great step forward when compared to its predecessors from the same

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manufacturer. The manuscript is generally well written. It gives a clear description of the major interest in the measurement of the derived isotopic quantities of d-xs and ^{17}O -xs. Measurement precision, instrumental drift, water concentration dependence, and calibration to reference materials are all described with clarity and mostly with sufficient detail. I recommend publication of the manuscript, after the authors have had the opportunity to clarify the issues raised here below.

P10192L9 and Article Title: Please use a more descriptive term than “current-tuned”, as practically all CEAS and CRDS schemes use laser current tuning of the laser. See also comment with P10201L11.

P10195L22: Correct year of publication is 2004.

P10196L2: It may be useful to refer the interested reader also to Aemisegger et al. (AMT 5, 1491, 2012).

P10196L12: With the exception of the very recent work by Berman et al. (2013), which is discussed later on, but could be mentioned here already.

P101999L8: Please explain what is meant with “external precision”. There appears to be nothing external to the determination of the measurement precision (=repeatability) on repeated samples. The same comment with your use of “external precision” on P10205L13: What does “external precision” mean here? I am familiar with the terms internal accuracy (instrument compared to itself or to a copy of itself) and external accuracy (instrument compared to an external independent standard), but would like to see an explanation or reference to what you mean by external precision. My guess is you mean that the precision of the isotope measurement is determined by a (long) time series measurement of a single sample, as opposed to a measure of the baseline optical noise (NEAS) of the spectrometer, but I am not sure, and I am afraid this is so for most readers. Worse, some may mistakenly interpret it as a “calibrated precision” (sic) or (an estimator of) accuracy.

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P10199L26: 1389 nm, considering the wavenumber is specified to four significant digits.

P10200L8: Please specify whether you use one (N₂) or the other (air), and especially if the measurement is immune to changing the matrix (which I expect it is not without modification of the spectral fit).

P10200L9: Personally, I prefer seeing the SI unit of hPa (=mbar); 50.0 mbar = 66.7 hPa.

P10201L11: It is clear that the relatively small Picarro cavity results in a rather large FSR of 600 MHz. As Figure 1 shows, this results in only 2 to 3 datapoints per FWHM of the ro-vibrational transitions. For many readers this may be construed as a very poor sampling of the spectrum. You may want to point out here explicitly that this is still sufficient due to the precise frequency scale: there is very little noise on the horizontal scale of the spectrum (provided the stability of the cavity is not compromised by, e.g., thermal or electrical noise on the piezoelectric mirror translator – see last comment here below). In addition to the almost perfectly equidistant frequency scale, it is important to point out that each datapoint has a well determined frequency resolution corresponding to the width of a cavity longitudinal, TEM₀₀ mode, equal to the FSR divided by the cavity finesse. It is thus interesting to know the finesse of the cavity. Related to this: what is the empty-cavity ring-down time, and thus the effective optical path length? In addition to this, please specify the NEAS (minimum detectable absorption normalized to bandwidth –measurement rate– and path length) for the three different instruments. This would allow a direct comparison of the spectrometer-only to other spectrometers that have been described in the literature. See, e.g., the discussion of different spectrometer figures of merit by Moyer et al. (APB 2008). It is for the time being of little use to be referred to the patent application as the text is not yet public. Although the authors make no such claim, the patent application suggests that the applied techniques are highly innovative. This may be true for the application in a Picarro spectrometer, but this is certainly not the case for the principles themselves. In

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fact, the "mode-by-mode" excitation of a cavity enhanced spectrometer is at the basis of FS-CRDS as introduced by Hodges in 2004, as well as of OF-CEAS, first published by Morville et al. in 2005. These works should be referenced in the current paper. The work of Hodges in particular may have implications for the defendability of the patent application presented here.

P10201L17: Again, it should be noted that, even though this may present a "critical innovation" for the Picarro spectrometer, the OFCEAS H₂O-isotope spectrometers built by us have been using this peak-area data analysis procedure since their inception in 2003 (mentioned in Kerstel 2004; first instrument publication in 2006 by Kerstel et al. in APB), as well as by the FS-CRDS instrument of Hodges and co-workers, and a number of other instruments. Please provide appropriate references.

P10202L11: Although the difference may not be large enough to be clearly identifiable, I am curious: Why the "soft-collision" Galatry model instead of the "hard-collision" Rautian-Sobelman or the Nelkin-Ghatak lineshape models? After all, the perturber (N₂) has a higher mass than the spectroscopically active H₂O molecule. Moretti et al., JMS 2000, argue for a "hard-collision" model for H₂O lines at 1.4 micron.

P10205L13: see comment with P10199L8.

P10207L5: To me the fact that the deuterium concentration dependence has not changed is an indication that the concentration dependence is not primarily due to residual pressure broadening effects, but rather to an incomplete accounting for the dependence of the baseline structure on the water concentration (J. Landsberg, "Development of an OFCEAS laser spectrometer for water vapor isotope measurements at low water concentration", PhD thesis university of Grenoble and university of Groningen (in preparation)).

P10207L17: For sake of clarity, it would probably help to point out that 2 * 5 * 10 injections are carried out per water sample, for a total measurement time of 5000 sec (1h23 > 30 minutes...) (whereas only 40 injections are retained to calculate a "memory-free"

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result). I understand that no specific calibration strategy (ordering of sample and reference measurements) was applied, but this becomes clear only after reading your comment on the LGR ICOS instrument in the Discussion section of the paper. One common strategy is to bracket the unknown sample measurements with those of reference samples. Such a strategy essentially doubles the required measurement time, as typically the same series needs to be repeated for the reference water, in this case requiring another 5000 sec. Thus, the total measurement time for one calibrated result would then be equal to approximately 10,000 s, just within the stability time dictated by the AV curves of Fig. 3 for ^{17}O s and dD (and only slightly beyond that for d ^{17}O and d ^{18}O). In this case of “the first calibration experiment” (with 5 samples, of which two are used for the VSMOW-SLAP scale correction and three are treated as unknowns) the total measurement time is 25,000 s. The AV curves then show that at this point the drift of ^{17}O -xs is still negligible, but that the precision of the primary isotope ratios has degraded by a factor of two. The ^{17}O -xs AV curve is actually ill-determined for longer times. Therefore, your experiment, which must have taken circa 7 hours, is also about the longest duration experiment that can be safely performed without having to worry that drift will start to degrade the measurement accuracy. In the calibrated error (accuracy) discussion I am missing a discussion of the propagation of the error of the reference water measurements (standards) on the VSMOW-SLAP scale correction, and thus on the accuracy of the isotope values of the unknown samples. The use of the standard error for each sample measurement series (5000 s) is correct in the assumption of normally distributed noise. With a measurement time that approaches or exceeds the optimum averaging time of the AV minimum, this is no longer true. This is in contrast to the situation of the measurements reported in Table 2, as I assume that, e.g., a VSMOW-SLAP calibration was carried out for each of the 6 determinations of GISP that were used to produce the averaged value and its standard error on the first row in Table 2. In this case the use of the standard error appears correct to me, as the mean value of the measurement does indeed become better known with each repeated calibrated measurement.

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P10209L2: bracket at the right place: “. . . per meg (Schoenemann et al., 2013).”

P10209L14: σ_{18} instead of second mention of σ_{xs}

P10221FIG1 I find it highly surprising, in light of the cavity FSR being fixed, that the measurement points are distributed as they are, sampling each line (all three of them in the case of laser 1) symmetrically with a central datapoint at the maximum of the line. This cannot be accidental. Is there still a piezo on one of the cavity mirrors able to adjust the cavity length? Can the L2140-i thus switch between mode-by-mode scanning and the traditional Picarro WS-CRDS mode of operation (turning it into an L2130-i-C)? Is this piezo used to move the cavity frequency comb in between spectral scans? If so, doesn't the bias applied to the piezo lead to an even further reduction of the thermal stability of the cavity? Please explain . . .

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 10191, 2013.

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