

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.

Anonymous Referee #2

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The paper presents an improved version of a commercial optical water isotope analyzer produced by Picarro. This follows on to similar efforts for a competing commercial product made by Los Gatos Research and published in Berman et al. (2013). The new analyzer uses an improved laser stabilization method to achieve precisions similar to mass-spectrometric reference methods.

The paper describes the method and results satisfactorily, but needs clarification and correction in the points listed below.

General comments:

The term "accuracy" should not be used in the context of this paper because, from a metrological point of view, none of the measurements are traceable to the SI. They

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all depend on calibration against conventional delta values of the reference materials VSMOW and SLAP (i.e. delta values that have been fixed to a certain value for convenience, to eliminate scale variations between different laboratories). The term "reproducible" may however be appropriate: results give numbers that reproduce results from other labs, after two-point normalization. To establish the accuracy of the results, a careful calibration of the instrument using gravimetric mixtures of pure (or at least enriched) isotopologues would be required. See also VIM3 - International Vocabulary of Metrology (<http://www.bipm.org/en/publications/guides/vim.html>).

Please explain whether the results in Table 2 include the calibration and normalization uncertainty from the analyses of SLAP vs. VSMOW.

Results for both the commercial and the custom-built vaporizer should be shown and compared.

Measured results for $\delta(18\text{O})$, $\delta(17\text{O})$ and $\delta(2\text{H})$ for SLAP vs. VSMOW should be shown before normalization to demonstrate how large the scale compression is compared to the conventional values of -55.5‰ , -29.7‰ and -428‰ .

A scatter plot of $\ln(1+\delta(17\text{O}))$ vs. $\ln(1+\delta(18\text{O}))$ prior to normalization should be shown for the CRDS data in Table 2 as well as the data from the corresponding IRMS measurements (currently not shown anywhere). What are the corresponding slopes of the plots? This would add important information about the nature of systematic instrumental errors, in addition to what has been included in the Discussion section and Figs. 7 & 8.

The paper by Berman et al. (2013) should be referenced already in the Introduction, not only in the discussion.

The differences to the analyzer used by Berman et al. (2013) should be explained.

SI units should be used. Replace Torr with Pa or mbar. sccm (p. 10200) with $\text{cm}^3 \text{min}^{-1}$ and give the relevant conditions (273 K, 1 bar?).

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^{17}O excess is a compound noun, so "excess" should be written as subscript index to " ^{17}O ".

Specific comments:

10192/12: According to fig. 4, 40 measurements took 60 h, so 1 measurement should take 1.5 h, not 30 min, which is not significantly faster than the mass-spectrometric method, which takes 2.2 h (Barkan and Luz, 2005).

10192/15: It is not clear how "precision" is defined - repeatability of multiple injections of the same sample, continuous measurement of a single sample over a long time, reproducibility of an isotope delta on different days (i.e. including calibration).

10197/9: Eq. 6 is wrong. The right hand side needs to be divided by $(1 + \delta^{18}\text{O}_{\text{raw}}^{\text{VSMOW}})$. However, this error is inconsequential because it cancels out in the next step (Eq. 7).

10198/1: This statement is only correct if the measured values are normalized according to their measured delta ^{18}O values and a corresponding clarification should be added.

10200/1: Give the values for sigma here. The stated precision (standard error) is the expected precision based on Poisson statistics, not necessarily the standard error that can be achieved under realistic conditions.

10200/10: This is not a concentration, but a mole fraction. SI units should be used, i.e. 20 mmol mol $^{-1}$ or similar. How close does the actual concentration need to be to its nominal value of 20 mmol mol $^{-1}$?

10202/5: Compare and contrast this measurement principle to that used by Los Gatos Research in their instrument (Berman et al. 2013), which also uses a peak integration method.

10208/1: Please clarify whether seawater samples can be analyzed with the analyzer

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and if so, what precautions need to be taken.

10210/16 & Figs. 7 and 8: Please explain what you mean by "residuals" and how the residuals have been calculated.

10211/15 & Fig. 5: Please extend Fig. 5 to 5000 ppm to demonstrate the claimed linearity of the correction.

10211/22: Please cite Barkan and Luz (2005) as reference for the equilibrium value of 0.529.

10212/18: Delete sentence starting "Direct analysis of ambient water vapor ..." as this has not been demonstrated and cannot be a conclusion of the paper.

10212/22: Please tone down the language - if any paper has "established" CRDS measurements of ^{17}O excess as alternative to IRMS, then the paper of Berman et al. (2013) should be cited.

Fig. 1: Explain what fit function was used for the peaks.

Table 1: It is unclear what you mean by standard error. For example. for GISP, is this the standard deviation of the 20 individual (daily?) results, i.e. the standard deviation of the mean? Or the mean of the standard error of the 20 individual results? The former value would be more informative, but should be called "standard deviation of the mean", for the avoidance of doubt.

Technical corrections:

In species such as H_2^{18}O , the subscript 2 and superscript 18 should be separated to make clear which atom the indices belong to.

10192/22: The element symbol is missing on the left hand side of the equation, e.g. $\delta^{17}\text{O} = \dots$

10192/23: The physical quantity " ^2H ", " ^1H ", etc. refer to needs to be included, e.g.

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isotopic abundance x or concentration c , so that $2R = x(2H) / x(1H)$, etc.

10193/3: The center dot should be deleted.

10193/19: Define $n\{^0\}$.

10193/21: The indices should be "sample" and "reference" to be consistent with equation 1. They should be in upright font.

10193/24: This applies only to equilibrium for T approaching infinity.

10194/2: $\lambda = \ln(Q17/Q16)/\ln(Q18/Q16)$. Instead of nuclide numbers, exact atomic masses should be used so that $\lambda = 0.5305$.

10194/14: The center dot denotes a scalar product of matrices and should be deleted.

10194/17: A reference needs to be given.

10194/19: The crosses should be deleted or replaced by an equal sign.

10195/13: 30 min (Barkan and Luz, 2005)

10197/9: The index should be "sample" for consistency (see above).

10197/11: The left hand size should show $\delta^{18}O$.

10200/2: Delete tilde sign (\sim) - the number of significant figures should be chosen so that the value reflects its uncertainty.

10200/6: Delete tilde sign.

10201/19: Add "molecular" before monochromatic and delete "molecule-1" from within the parentheses. The units of κ should be $\text{cm}^2 \text{Hz}^{-1}$ (based on Eq. 10).

10201/22: The center dot should be deleted.

10202/13: The symbol "Re" should be used to designate the real part of the imaginary number. A single R with a left bar designates the set of real numbers.

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10203: All equations need to indicate the measured quantity on the right side, e.g. $18R = A(\text{H}218\text{O}, 11) / A(\text{H}216\text{O}, 2)$.

10204/11: Replace "Tee" with "tee union" (lower case, no quotation marks).

10204/16: Replace concentrations with mole fractions.

10210/6: Delete equal or approximately equal sign.

10211/5: What does "approximately 100" mean? 99? 100? 80? 120? Do you need the approximation sign?

10212/12: Replace "deviation" with "difference".

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

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