

## ***Interactive comment on “On the reproducibility and repeatability of laser absorption spectroscopy measurements for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotopic analysis” by D. Penna et al.***

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First of all, the authors wish to thank Doug Baer of Los Gatos Research Inc. for reading and commenting the manuscript, which we believe will help clarify some crucial points and improve the final version of the paper. Comments are quoted above the authors responses.

1. “When quantitatively describing precision, it is important to distinguish between the standard deviation for each injection and the instrument’s analytical precision. Generally, each measurement of a liquid sample (whether it is of an unknown sample or a reference standard) involves 6 repeated injections, of which the first two injections are

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discarded (typically) and the last four injections are averaged. The values reported in the Abstract (line 17) and inside the manuscript represent the standard deviation for each injection and not the instrument’s analytical precision. In particular, in the sentence “analytical precision ranged from 0.56‰ to 1.80‰ for d2H and from 0.10‰ to 0.27‰ for d18O” refers to the precision of each injection, and not the precision of each sample measurement, or the overall instrument precision. To be consistent with earlier papers, as well as manufacturer specifications, the instrument precision should be described by the standard deviation of the complete sample measurement, which is the mean of the four injections, as reported in Aggarwal et al. (2006), Lis et al. (2008), IAEA (2009), Lyon et al. (2009), and Berman et al. (2009). Thus the standard deviation of the mean of the four injections will be two times better than the reported values for each injection.”

We fully agree with the clarification that “the instrument precision should be described by the standard deviation of the complete sample measurement, which is the mean of the four injections”. Indeed, this is what we have done in the study. As mentioned in the manuscript, according to scheme (A) (IAEA, 2009), for each sample we performed 6 injections: two were discarded and the mean and standard deviation of the remaining four injections were computed. The mean represents the sample reportable delta value and the standard deviation the precision of the sample measurement. To assess the overall instrument precision, the mean of standard deviations over 49 samples with a wide range of isotopic content was computed. The mean of standard deviations, along with other descriptive statistics, was calculated for each laser spectroscopy and isotope species and was presented in Table 4. Therefore, the values reported in the Abstract (Page 2977, line 17) and discussed in Section 3.5 (Pages 2989-2990) of the manuscript do refer to “the precision of each sample measurement, or the overall instrument precision” averaged over the entire dataset. For major clarity for the readers, we will add to the manuscript a definition of instrument precision, as suggested by the comment.

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2. “The paper noted the Liquid Water Isotope Analyzer (LWIA) IV is a V2 analyzer (or “new version”). It should be mentioned that this second-generation Analyzer, which began shipping in 2009, provides 720 injections per day, three times the net throughput of the first-generation instrument, without compromising performance. Using the manufacturer’s recommended measurement sequence that consists of one reference standard before every three unknown samples, 720 injections allows measurements of 120 total samples, of which 90 measurements are of unknown samples and 30 measurements are of reference standards. Thus the second-generation instrument allows users to select to report data at this fast rate for applications requiring high temporal resolution (e.g., for time-resolved measurements in streams or precipitation) or to average repeated measurements to obtain even higher precision, if desired.”

As mentioned, only one of the four laser spectrometers that were considered in this study was a second generation (version 2, V2) analyzer. In the manuscript, we mentioned the faster performance of the V2 analyzer compared to V1 (Page 2993, last lines). Specifications in the V2 user manual (Los Gatos Research Inc., 2010, Page 67) state that each injection typically requires around 120 seconds (and this was also verified in the analysis runs) whereas injection time for V1 analyzer is around 250 seconds. This means that the V2 analyzer is slightly more than twice faster than a V1 analyzer. Thus, one could analyze 90 samples and 30 reference standards by means of a V2 analyzer following the manufacturer’s recommended measurement sequence (one reference standard before every three unknown samples) but this was not tested in our comparative study. We applied the same analysis scheme to analyzers V1 and V2 but the test did not show statistically significantly better results for the V2 analyzer. Nevertheless, it should be noted that only one V2 unit was tested in this study and the obtained results might be subject to individual laboratory conditions. We found, when applying the analysis scheme (A) suggested by IAEA (2009), that a double amount of samples and standards (i.e., 60 and 30, respectively) can be determined with a V2 analyzer compared to a V1 analyzer. Besides faster runs, other advantages of the V2 spectrometer comprise decreased maintenance requirements, the possibility of longer

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runs, longer syringe lifetime due to improved heater and stronger septa, thus less user interference and performance costs.

3. “The standard deviations of the differences between the IRMS and LWIA (Table 6) are consistent with the convolution of the IRMS uncertainty ( $\pm 0.7\%$  for d2H) and LWIA uncertainty ( $\pm 0.6\%$  for d2H). Without noting this, a casual reader may inadvertently assume that these standard deviations of the differences are solely due to errors in the LWIA.”

As stated in the manuscript (Page 2992, lines 16-18), Table 6 presents the basic statistics of the maximum difference between repeated measurements of hydrogen and oxygen and not the standard deviations of the differences between the IRMS and LWIA, as reported in the comment. In our comparative study, we analyzed a subset of seven samples three times (in three separate vials) during the same run to assess the capability of the LWIAs to consistently reproduce isotopic ratios of the same sample. Then, we computed the difference between the maximum and the minimum value obtained from the three repeated measurements of the same sample to assess the widest range of isotopic values derived by the repeated analysis of a single sample. We followed this procedure for each sample of the subset and for each of the four spectrometers, for both hydrogen and oxygen. Finally, we reported (Table 6) the basic statistics (mean, standard deviation, minimum, maximum) of the maximum difference among the three repeated measurements for the entire subset of samples. We concluded that (Page 2992, lines 23-29) “Overall, the capability to reproduce comparable results from the analysis of repeated samples was acceptable with differences between the maximum and the minimum values which were generally within the range of the standard deviation yielded by the single measurements. [...] Nevertheless, in some instances, the repeated measurements of the same sample were relatively different with marked unsteadiness and randomly distributed inconsistencies.”

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