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

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This manuscript presents a thorough inter-comparison of four Liquid Water Isotope Analyzers (Los Gatos Research) that includes three first-generation (model 908-0008) instruments and one second-generation instrument (model 908-0008-2000) and, as stated in the manuscript, confirms all instruments meet or exceed manufacturer specifications. We applaud the careful work by the authors and appreciate the opportunity to offer some comments on measurement precision, sample throughput, and overall relative uncertainty.

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 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 \( \pm 0.56 \)‰ to 1.80‰ for \( \delta^{2}H \) and from \( \pm 0.10 \)‰ to 0.27‰ for \( \delta^{18}O \)” 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.

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.

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 \( \delta^{2}H \)) and LWIA
uncertainty (± 0.6 ‰ for δ2H). Without noting this, a casual reader may inadvertently assume that these standard deviations of the differences are solely due to errors in the LWIA.

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