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Hydrology and Earth System Sciences Discussions

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

B. Newman (Referee)

b.newman@iaea.org

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Review by Brent D. Newman and Luis Araguas-Araguas, IAEA Isotope Hydrology Section, June 22, 2010.

General Comments: The paper describes comparison testing between four laser absorption based stable isotope analysers and IRMS. Given the increasing popularity of these instruments for hydrological and other investigations the manuscript is quite timely and should be of interest to the HESS readership. Overall, the paper is well written and the discussion of the results is quite comprehensive. We suggest that the

manuscript be accepted for publication after due consideration of the review comments below.

Specific Comments: Pg. 2979, top: Results in IAEA (2009) were generated using multiple analyzers. However, no systematic comparison was done between the different instruments.

Pg. 2981 index 5: Sentence should begin with "The manufacturer provided . . ."

Pg. 2981, top: It is our understanding that the manufacturer supplied standards are intended for initial testing purposes during installation of the instrument. It is unclear what the pedigree of these standards are and how well their isotope compositions have been characterized. Given the results of this paper, as well as being familiar with others who have used these standards, it is clear that they are not far off. Use of these standards shouldn't impact the relative differences between the 4 instruments, but the resultant values could be impacted especially for comparison of laser based results to IRMS. Some discussion of this issue should be provided.

Pg. 2981, top: It is reasonable to use IRMS as a basis for comparison. However, there is little information provided about how the IRMS values reported were derived, how much replication was involved, and whether the very negative standards have been normalized to the V-SMOW/SLAP scale to account for scale effects (See Coplen, 1998, Chem. Geol. 72(4)).

Pg. 2981, between 20 and 25: The control standard is not a preliminary indicator of run accuracy, it is the primary indicator of run accuracy because it is the only standard that is run blind and not used in calibration. Thus, it is the only robust way to evaluate accuracy during a run.

Pg. 2983, 20: insert "values" between spectrometer and for

Pg. 2884, line 1: suggest using curve instead of bell

Pg. 2985, section title: discussion should be singular

Pg. 2985 last line: delete “good”

Pg. 2987 bottom and 2988 top: for the extreme values, memory effects can be substantial as discussed in IAEA (2009). Thus, the procedure of throwing out two values may not adequately reduce memory effects during analyses of extremely negative samples. Were special procedures used to address the memory effect problem with these extreme samples? Also, how were calibrations performed for the extremely negative values? Might this be part of the reason for the observed bias with deuterium? We find the deuterium result curious because even though these are what would be considered extreme values in delta space, they are not in terms of absorption space (where one might expect responses to still be quite linear). We would have expected smaller deviations for deuterium based on this and our experience in analyzing extremely positive values (see comment below).

Pg 2988 top: You could consider mentioning the results of IAEA (2009) where laser based analyses of waters up to ∼+1670 ‰ ïĄď2H and +14 ‰ ïĄď18O gave comparable results to IRMS suggesting that the instruments may be satisfactory at least on the positive side of the scale.

Pg. 2989: It would probably be worth noting that the precision results reported in Aggarwal et al. (2006) were from a prototype version of the instrument and did not have the same configuration as used in the more recent studies.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 7, 2975, 2010.