

Authors' responses to the comments of reviewer#3, Fabio Marzaioli

Thank you for reviewing and commenting on our manuscript “Technical note: A fast and objective autosampler for direct vapor equilibration isotope measurements”. We found the advice constructive and will incorporate the suggestions into our revision. We've responded to each comment individually below.

The authors have developed an automated system, called VapAuSa, for water isotope measurements by direct vapour equilibration (DVE-LS). The system is described with a lot of detail, but the data reporting and commenting is still poor in my opinion. I see a strong problem in the definition of accuracy and the results obtained are hardly commentable in this sense. The data are there, but some work should be done to produce scientifically meaningful results.

Detailed comments.

Abstract

Ln 7: What do the authors mean for lack of objectivity?

In regular direct-vapor-equilibration laser-spectroscopy (DVE-LS) measurements, the measurements fluctuate during analysis. The operator has to subjectively decide when the measurements look stable, and then note the analyzer readings.

Ln 12: Can you please specify what is your precision estimator? Are they comparable according to a Fisher test?

We will change the accuracy metrics to repeatability (applying standard deviation) and measurement bias (average difference of measurement to true value).

Intro

Ln 29: I would suggest not using “isotope analysers”. It goes in the verse of a measurement black box while if one knows principles of measurements for apparatuses can be a great help to produce accurate data.

We will avoid using “isotope analyzers” and change it to the accurate device description (cavity ring-down spectroscopy (CRDS) or laser spectrometer)

Ln 29: Please avoid the usage of isotopic composition (refer to isotope ratio δ).

We will change the wording to the scientifically correct terms.

Ln 32: Please rephrase, how does a vial contain vacuum? The whole process happens under vacuum.

We will discard the whole part on cryogenic extraction to focus more on direct-vapor-equilibration.

Ln 37: add Gas before tight.

We will adapt the wording.

Ln 38: I would not see the 2) as a different point form the 1).

We will summarize both under point 1)

Ln 42: Isotopically Equilibrate: change to “can reach isotope equilibrium”.

We will change the wording to your suggestion.

Ln 49: volumessimilar: volume similar?

We will correct that.

Par 3.1

Ln 123: 3 not three.

According to the HESS style guideline we will leave it at three (“For items other than units of time or measure, use words for cardinal numbers less than 10; use numerals for 10 and above (e.g. three flasks, seven trees, 6 m, 9 d, 10 desks)”); <https://www.hydrology-and-earth-system-sciences.net/submission.html#english>).

Table 1: Tables can not be used without IS units.

Good point, we will fix that.

Period starting at line 130: There should be uncertainties for the reported water samples. Only primary standards are reported with no uncertainties.

Thank you for pointing this out; the uncertainties are only shown and stated in figure 5. We will add it to the text.

Ln 135 and soon after: Accuracy cannot be a difference between 2 values. Of course, since a and l are measured, they are affected by uncertainties. Therefore, an unbiased way to define accuracy is to define a variable whose numerator is the reported difference (accuracy d18O formula) and whose denominator is the propagated uncertainty of such a difference.

We now calculated measurement repeatability by applying standard deviation for the identical samples, as well as calculating the measurement bias (average difference of measurement to true value) for the whole system. This should produce a more robust statistical assessment.

Par 4.1 (Accuracy)

The section is not homogeneous. The introductory part should be included in the intro. Also, if some authors (Ln 170) used repeatability as an indicator of accuracy, it should be stated that this is a misinterpretation. Also, it is not a matter of ranking accuracy vs repeatability, they are 2 different concepts.

We will introduce the section already in the intro. Yes, no uncertainty metric is inferior to the other, however we think some are better suited to assess the performance of a new device than others. Measurements can be highly inaccurate even when repeatability is high. Ideally, authors should state both metrics.