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## Comment on amt-2022-230

Anonymous Referee #2

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Referee comment on "Optimization of a Picarro L2140-i cavity ring-down spectrometer for routine measurement of triple oxygen isotope ratios in meteoric waters" by Jack A. Hutchings and Bronwen L. Konecky, Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2022-230-RC2>, 2022

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Review of Optimization of the Picarro L2140-i Cavity Ring Down Spectrometer for Routine Measurement of Triple Oxygen Isotope Ratios in Meteoric Waters" by Hutchings and Konecky, AMT.

### General:

The manuscript presents an in-depth investigation of potential problems and an improvement in detecting and correcting these through optimizing the analysis of the raw data and adjusting the measurement series setup. This problem is particularly relevant for the secondary isotope parameter  $D^{17}O$ , as this parameter is strongly influenced by spurious spectra of various organic molecules, as the authors show using water standards spiked with alcohol. I like their approach and was surprised that they even observed significant shifts of  $D^{17}O$  in rainwater due to such influences. The manuscript should be published in AMT as it discusses important problems with this analytical method and suggests remedies that should be known in the scientific community.

### Major points:

It would be interesting to know how the samples were stored. Which containers (material, colour), caps and membranes were used and how long were they stored before analysis? This could be important for the development of organic substances in the sample container.

Since the analysis time for high-precision measurements per sample - as suggested by the authors - is very long at 6.3 hours, it would make sense to first run the sample value

range with a 1-injection sequence and order them according to the pre-measured values. This would minimize the memory effects and could therefore lead to a shorter total time.

Why was the BSM and not the ANT standard used as the second normalization standard, the latter standard would be most negative for both the  $d^{18}\text{O}$ ,  $d^{17}\text{O}$  and the  $dD$  that you have available. Your choice requires extrapolation of your normalization for highly depleted samples, but I suspect that you have not measured any such samples other than the ANT standard.

It is not clear how the memory effect for  $D^{17}\text{O}$  was calculated, as this cannot be calculated directly from a simple  $D^{17}\text{O}$  balance, as it relates to a difference in logarithmic values. Please add a sentence on how this was done.

The memory effect has been calculated based on alternating the Kona and ANT standards, i.e. an enriched and a depleted isotope value from which percentage memory influences are calculated. This is correct, but this leads to different times for reaching the instrument noise level as the differences among the samples will be significantly smaller for all isotopes. Therefore, an ordering according to their pre-measured or estimated sample values could most probably lead to a significant reduction of the overall time investment without losing precision. See also a minor comment to Fig. 6 below.

I don't quite understand why they used a particular standard for drift correction. Would it be possible to use one of the other four standards you have in use?

### **Minor points:**

P5            Table 1 legend: something is missing....by this....

P6            Is there a reason why the vial position is different for the standards but not for the MCM QAQC sample (vial position 1 for both the first and last measurements)?

PXX           the formatting of  $d^{18}\text{O}$  and  $d^{17}\text{O}$  is not consistent, check the complete text.

P15, I324ff You have measured an unknown sample several times distributed over several series and months. Have you measured the sample water in the same vial? Have you recapped the vial after each measurement sequence? Or have you measured the same water sample by decanting it into individual vials every time you measured it? The procedure is not clear to me it but should be mentioned.

Fig. 6 I guess that the values shown depending on the previous sample or standard value measured or is this no issue? The mean absolute error may indicate that it is dependent on the various sample. The accepted value of the current sample is reached either from below or above this value. Therefore, one would have to indicate based on which jump (current to previous sample or standard) these values shown in Fig. 6 are based. The absolute error then depends on this jump. This should be mentioned.