

Review of AMT Paper – May 20, 2023

“SI-traceable validation of a balloon-borne spectrometer for water vapor measurements in the upper atmosphere”

By

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This is an impressive study which describes a newly developed QCL-based absorption spectrometer for highly accurate balloon-borne water vapor measurements in the UTLS. The instrument was validated in the laboratory employing SI-traceable reference gas standards from: a dynamically diluted gravimetric permeation system; and from gravimetrically prepared compressed gas water vapor mixtures. Various absolute water vapor mixing ratios from 2.5 ppm up to 180 ppm were generated and measured over the range of temperature and pressure conditions representative of the UTLS.

Using these standards, improved spectroscopic broadening and pressure shift parameters were determined employing a quadratic-speed dependent Voigt fitting profile, which accurately reproduced the measured line shapes without systematic residuals over the entire pressure range. The resulting fitting approach and empirically determined parameters improved the resulting accuracy over the more traditional Voigt line profile using HITRAN 2020 parameters. The authors clearly demonstrated that their balloon-borne instrument is capable of retrieving UTLS water vapor mixing ratios with a calibration-free instrument with an absolute accuracy to better than $\pm 1.5\%$ with respect to the SI-standards.

The results of this study and the future deployment of this instrument will represent a significant advancement in UTLS measurements of the most important Greenhouse gas. This paper is Excellent in its: Scientific Significance, Scientific Quality, and the Quality of Presentation. This reviewer highly recommends publication with only minor revisions, as detailed below, for improved clarity.

1. In the Abstract, it would be desirable to define the acronym ALBATROSS
2. Line 18, page 2: It would be useful to the reader to indicate right up front to write: “The aim of this work is to validate the accuracy and precision of a newly developed **open path** mid-IR quantum-cascade
3. Page 3, Starting on Line 13 in the discussion of “Rapid spectral sweeping ...”, although this approach is discussed in Graf et al. (2021), it would be useful for the reader to add another sentence right after “...Liu et al., 2018) further explaining this approach here. For example, you could add “ In this approach the laser driving current is applied in pulses, followed by a moment of complete shutdown of the laser to re-establish its initial temperature”.

4. Regarding Fig. 1, I am a little confused by the conceptual diagram of the solenoid valve following the diluted permeation source. I would expect the common port on the MFC3 end and not on the Zero air input end. Also, I was expecting a multi-port valve whereby the diluted permeation flow is directed out to a vent port without flow disruption when the Zero air is switched in. I realize this is a conceptual diagram, but it would be important for clarity to represent this more accurately.

Also, for completeness the authors should mention whether or not they observe any hysteresis in the time response passing through MFC3 into the MP cell upon switching in and out the diluted permeation flow and the Zero air. Is the 3 hour equilibrium time dictated by hysteresis in this MFC, by the MP cell, by the connecting lines, or all of the above?

Also, a brief discussion of the actual liquid water source used in the permeation device and its purity is warranted

5. Table 1 headings and descriptor at the bottom, needs further clarification/modification. The labels “Nominal value” and “Actual value” need to be defined more clearly in the descriptor below. These terms refer to the generated water vapor mixing ratios from the dynamic-gravimetric method and the spectroscopic measured values, respectively. The descriptor “expanded measurement uncertainty” is confusing here, as I believe you are combining two terms: the expansion in the number of significant figures in the determined spectroscopic values from the nominal values expected from the generation system and the combined uncertainty from all the parameters employed in the spectroscopic measurement? Is this correct. Are these uncertainty limits at the 1σ levels? Do the nominal values from the standards generation system have additional significant figures than those shown in Table 1? I ask this because aren't you ultimately relying on agreement between your qSDVP fitting procedure and the standards generation system output (as implied on page 10, line 3)? If your absolute water mixing ratios from the standards generation system does not have more significant figures than those indicated in Table 1, aren't you reporting too many significant figures in your expanded actual values? Perhaps some clarification here?
6. The comparison between the polynomial baseline fitting and the empty cell approach is impressive and is important since only the former can be used in real atmospheric measurements.