

Interactive comment on “Measurement of low-ppm mixing ratios of water vapor in the upper troposphere and lower stratosphere using chemical ionization mass spectrometry” by T. D. Thornberry et al.

Anonymous Referee #1

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The manuscript by Thornberry et al. describes the set-up, characterization and application of a Chemical Ionization Mass Spectrometer (CIMS) which is designed for the measurement of water vapor in the upper troposphere/lower stratosphere (UT/LS) region. The measurement of the water vapor concentration in this part of the atmosphere is of great importance for the understanding of cloud microphysical process, especially with respect to the formation and properties of ice particles in cirrus clouds. Both, in-situ as well as remote sensing techniques have been applied on board of high altitude research aircrafts. However, for many years there has been a substantial disagreement

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between these instruments although some of them (like the chilled mirror hygrometer technique) make use of an absolute measurement of the water vapor concentration. Calibration and comparison of the different instruments on the ground generally yields a better agreement. This fact points to the presence of unrecognized artifacts in some instruments having a larger impact when these instruments are operated under the cold, dry and low pressure conditions in the UT/LS region. In order to identify such artifacts in-flight calibration is required, as pointed out by the authors. However, up to now such calibrations have not been performed routinely in any of the instruments. The method described by Thornberry et al. overcomes this lack and their CIMS instrument includes a sophisticated calibration scheme which utilizes two different sources to generate known concentrations of water vapor which can be injected into the inlet. The concentration of the water vapor is determined by measuring the signal of H_3O^+ ions with a quadrupole mass spectrometer.

The manuscript is well structured and the method is thoroughly explained. The instrument characteristics are described in great detail and the results presented give strong confidence that the method yields accurate and precise results. Especially the calibration part allowing the in-flight calibration represents a big step and will very likely help to gain more confidence in the measurement of water vapor in the UT/LS region. Since the calibration scheme is not restricted to be used in combination with a CIMS instrument other groups will possibly adopt it. Therefore, I strongly recommend the publication of the manuscript in AMT.

Some points which should be addressed are listed in the following:

Page 389, line 4 (and also line 25): Why are the standard 210Po not suitable for the operation at lower pressures and flow rates? It would be nice if this could be explained in one or two sentences.

Page 392, line 13: “flows (0-20 sccm each)”: the flows indicated in Fig. 1 are somewhat different

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Page 392, line 27: How is the [H₂O] in the zero air known ([H₂O] is used to denote the water vapor concentration)? What is the exact water vapor concentration in the zero air? Throughout the manuscript, mostly a range between 0.5 and 0.8 ppmv is stated (e.g. Fig. 1; page 396, line 11; page 398, line 7). However, at other places (e.g. Table 2; Fig. 5, lowest calibration point) it seems that this range is much smaller and that the zero air water vapor content is much better defined as the range from 0.5 to 0.8 ppmv suggests. It should be made clear whether the range refers to the variation in [H₂O] for different zero air gas bottles, or if it is due to the uncertainty of the [H₂O] in one zero air gas bottle.

Page 396, section 3.1.3: A chilled mirror hygrometer (MBW) is used as the reference instrument for the calibration. Therefore, the question is why the MBW is then not used in combination with the calibration system during the flights. As it is demonstrated later (from the data shown in Fig. 11 and Fig. 12) it becomes clear that the CIMS instrument has some important advantages over the MBW in terms of precision and time response. Therefore, it might be useful to point the reader already to these benefits in section 3.1.3 to avoid confusion.

Page 399, line 13: There seems to be a typo in “in quantities to that produced H₂O mixing ratio”.

Page 401, line 27: It should read “descended back to 13.9 km”.

Page 403, line 9: It is not clear what the word “instrument” refers to here. Do the authors mean the vacuum chamber of the mass spectrometer?

Page 418, Fig. 8: Two of the steps in region IV show rather large spikes in the H₃O⁺ signal. Where do these come from and can it be ruled out that they influence the calibration curve?

Table 2: It would be good to state also the overall uncertainty (systematic and statistical error) in the measurement.

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Fig.2: Indicating the direction of flight would be beneficial.

General comment: The unit “ppmv” should be used consistently (as in Fig. 5), this is not always the case (e.g. “ppm” in Fig.6).

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