

Anonymous Referee #3

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Review of "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.

The authors thank the reviewer for providing constructive comments on the manuscript. Our responses to the individual comments are included below and changes to the text are indicated.

Comments:

-The non-linearity of the ion chemistry (and thus requirement of nonlinear calibration curve) is perhaps the only major drawback of this methodology. Assessing the overall variance in the calibrations is therefore important for the reader. Toward this end, it would be useful to show the entire set of calibration points on a single figure, along with the statistical parameters that describe the variance in sensitivity across each calibration level. From such an analysis, extrapolated calibration for the first 1+ hours of the flight may be possible, albeit with higher uncertainty.

A second panel has been added to Fig. 9 (now Fig. 10) showing the various calibration curves observed in flight along with the ground calibration curve from Fig. 5 (now Fig. 6).

The intractability of recovering the first portion of the flight is that both the calibration and sample lines were subject to parasitic water, but to different extents. Reasonable, approximate values can be calculated using calibrations from later in the flight, but the induced uncertainty makes this not worthwhile.

-It is a bit surprising that no normalization is used to account for variation in total ion transmission. Is the variation in sensitivities for a given calibration point reduced if the H_3O^+ signal is normalized to total ion current, or even say, the O_2^+ signal? The total ion transmission may contain short-timescale variations arising from potential and pressure drifts, as well as long timescale changes such as detector response, and changes in ion source characteristics; though, in the case of source material Am-241 with half-life of 432 years, no noticeable change in the source activity should occur in the lifetime of this instrument, precluding spillage and displacement of the radioactive material.

An initial plan was to use the NO^+ signal to normalize the H_3O^+ signal as NO^+ is largely independent of H_2O , while O_2^+ and total ion current were observed to not be completely conserved. Unfortunately, optimal operation required different quadrupole parameter settings in the m/z 16-22 mass scan window and the m/z 27-44 window, which resulted in differences in the variations in peak position and transmission between the two windows. This rendered such a normalization non-useful. Text discussing this has been added to section 2.3.1.

-The quadrupole power supply stability was not discussed in the paper, but only indirectly alluded to in the discussion of monitoring variation in peak shape. Typically, the tuning of these power supplies is a strong function of their ambient temperature, and with the instrument being housed in an unheated cargo bay, the question arises as to how well the temperature of the quadrupole power supply was controlled. Perhaps one way to respond to this question is to include a graphic showing the variation in the nominal maximum $m/z +19$ peak position taken from the high resolution scans which accompany the calibrations.

The temperature of the sealed HV/RF power supply enclosure varied slowly from 32 to 36°C during the flight. The quadrupole was operated with a FWHM resolution of ~ 1 at m/z 19 and there was no observable variation in the peak position (nice flat top). Text was added to state that the temperature of the quadrupole power supply was regulated.

-Pg. 400 Ln 26- Pg 401 Ln7 – *It is nice to see the fast time response estimated from toggling the calibration. However, it needs to be noted that the calibration gas enters a system at a point 15 cm downstream from the ambient sample point, and thus this estimate of response time does not include the first 15 cm of the sample inlet.*

Text has been added to the section discussing inlet materials (2.2.2) quantifying the time response observed for the 50 cm lengths of tubing (at 500 sccm). Given those results, the extra length of uninterrupted tubing upstream of the cal gas addition point at a flow rate of ~ 1500 sccm in the inlet is not likely to increase the response time significantly—which is born out by the similar time constants determined from switching on the inlet zero air, which is located just 3 cm from the sample point.

-Pg. 399 Ln. 1 – *I feel the word 'indistinguishable' may not be the proper choice here, unless it is accompanied by some statistics.*

“Indistinguishable” was chosen (not “identical”) to indicate that a given calibration curve could not be identified by appearance as a laboratory calibration or a flight calibration. The calibration curves were sensitive to the ion source voltage, ion source pressure and ion optics voltages which were intentionally varied over time to and statistically describing the entire population of calibration curves is less meaningful. To provide context for the reader (response to comment above), a second panel has been added to Fig. 9 (now Fig. 10) displaying the various flight calibration curves along with the laboratory calibration curve from Fig. 5 (now Fig. 6) to show the similarity.

-Pg. 401 Ln 19-21 – *Just a suggestion: Are there any other 10 Hz observations on board the aircraft, that are correlated or anti-correlated variation with H₂O, which you can show along with the fast H₂O observations? Scattering? This might enhance and support this graphic.*

Correlation between instruments in significantly different locations on the aircraft at 10 Hz would be problematic, even if there had been rigorous time synchronization available, since the separation is on the same order as the sample spatial scale. A more careful analysis of the 10 Hz data along with high frequency met observations for certain flight segments is planned.

-Pg. 402 Ln. 27 - Pg 403 Ln 1 - Have you considered dynamic dilution?

Dynamic dilution was investigated with the laboratory prototype during early development of the technique, using both N₂ and O₂ to adjust the ion chemistry. Text mentioning this has been added to the discussion section.

-Figure 2: Perhaps it is useful to show the direction of flight on this graphic.

Flight direction indicator added to Fig. 2.

Typographical corrections:

Pg. 389 Ln. 1 - Should the word 'low' be replaced with 'high'?

No, the point is that without taking steps to reduce the sensitivity, the signal saturates at quite low H₂O mixing ratios, yielding a very limited measurement dynamic range.

Pg. 402 Ln 27 - Is there a word missing after achieve, e.g. perhaps 'adequate'?

The text has been changed to read "to achieve a high sensitivity and S/N while maintaining a useful dynamic range".

Figure 8: The shaded portions of this figure are not visible in my printed version of the graphic. Perhaps you should make this separation more differentiated, or also list these regions using the numbers.

The segments discussed are separated by vertical lines in addition to shading, and enumerated with Roman numerals near the top of the plot.