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Atmospheric
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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 #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.

Summary:

This careful work describes the development and field-deployment of CIMS instrument for precisely measuring the small, but critically important, levels of water vapor present in the upper troposphere and lower stratosphere (UT/LS) region. In addition, this work

includes the notable development of an H2/Pt/zero air calibration system for producing controllable mixing ratios of H2O by oxidizing H2 over a heated platinum catalyst in the presence of zero air.

After addressing the (mostly minor) comments listed below, I feel this well-written manuscript should certainly be published in AMT, as it represents an important step for moving the UT/LS science forward.

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.

–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 H3O+ signal is normalized to total ion current, or even say, the O2+ 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.

–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.

–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.

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

–Pg. 401 Ln 19-21 – Just a suggestion: Are there any other 10 Hz observations onboard 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.

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

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

Typographical corrections:

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

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

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.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 381, 2013.