

Interactive comment on “Catalytic oxidation of H₂ on platinum: a method for in situ calibration of hygrometers” by A. W. Rollins et al.

A. W. Rollins et al.

andrew.rollins@noaa.gov

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We thank the referee for the valuable questions and comments that are raised. As a result we have improved the text by adding a number of details on the methods used. Responses to the specific points are addressed below. For each point the quoted referee text is in bold, followed by our response.

I think the title of the manuscript is a bit misleading, since the article does not describe testing of the technique “in situ”. There are a host of technical hurdles to overcome for the implementation of this technique in flight, so I think it would be better to have a title that does not include the phrase “in situ” until this aspect has been proven.

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A similar suggestion has been made by referee #1, and we have changed the title of the manuscript accordingly.

Since the evaluation of the accuracy of the technique depends on knowing the inputs very well, the authors should say more about the calibrations of the various components of their laboratory system. For example, it is stated on p 3086, lines 19-20, that flow controllers are calibrated to an accuracy of +/- 1%, but nothing is mentioned about the accuracy and precision of the “standards” – the DryCal flow meters. Similarly, the authors state that the zero air was observed to contain less than 0.5 ppm H₂O, but they do not describe on what basis they know this.

The ± 1% accuracy stated for flow controllers is based on the ± 1% accuracy of the DryCal. A more significant description of the procedure for calibration of the flow controllers has been added on lines 104-113. All of the H₂O concentrations stated in this manuscript are based on measurements made with the MBW. This included measurements of water in the zero air used. Text added 115-116.

One of the challenges with any type of calibration technique is knowing its absolute accuracy. I find it curious that the authors have chosen to reference all of their work to one or two frostpoint hygrometers. While the MBW and FPH may be represented as quite accurate (reporting frostpoints to +/- 0.1 °C), they are also potentially subject to biases and these biases will then propagate into the new calibration system. The authors are surely aware that the in situ measurements reported by the NOAA FPH are nearly always at the lowest end of the range of in situ techniques and that many have questioned the accuracy of the frostpoint method because of concerns about this and the inherent errors in the various algorithms for converting frostpoint to mixing ratio. It would be nice to see checks performed on this new calibration technique against other methods for determining water vapor or for producing known amounts of water vapor.

The accuracy of the water vapor concentrations produced with our system is deter-

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mined by a) accuracy of the H₂ standards, and b) accuracy of the flow mixing and delivery system. Here we used frost point hygrometers only to verify that the expected concentrations of H₂O were produced. As noted in the manuscript (lines 246-248) one of the advantages of this system is that it is not only a convenient calibration system but also brings forward a new primary standard of H₂O based on gravimetric standards of H₂. For this reason the technique presented here would be appropriate for calibration of a frost point instrument.

We chose to use the frost point hygrometers for our reference standard because this technique is considered to be a fundamental and NIST traceable measurement of water vapor mixing ratio. It is true that in situ comparisons in the UT/LS between frost point instruments such as NOAA FPH and other techniques such as Lyman-alpha and absorption spectrometers have revealed significant discrepancies, but this has been shown to not be a problem in the lab where measurements agree to a much better degree (see Fahey et al.). In the lab where a frost point instrument can be operated under conditions such that the ice and vapor are unquestionably in equilibrium, and any potential chemical interferences can be eliminated, the accuracy can only be limited by the knowledge of the frost temperature, total pressure, and the knowledge of the temperature / vapor pressure relationship for hexagonal ice. To the best of our knowledge the frost point technique not been demonstrated in the lab to have fundamental flows that limit its accuracy. Text has been added (lines 149-154) explaining our choice in hygrometer.

Figure 2 would be more useful if the y-axis were % conversion rather than absolute H₂O amount

Figure 2 has been modified to show % conversion.

Figure 3 should show errorbars for the measured H₂O based on the uncertainty in the frostpoint measurement, plus the conversion from frostpoint to water mixing ratio

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The uncertainty in the MBW measurement is quite small (always less than 1.7% of the mixing ratio) and are much smaller than that of the calculated mixing ratio expected from the catalyst system. Therefore for clarity in the figure we prefer to omit these, and have noted the range of MBW uncertainties in the text (lines 209-211). Comment also added to figure caption noting omission of uncertainties.

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