

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

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We would like to thank the referee for the constructive comments and questions on our manuscript that have lead to improvements in the text. The manuscript has been revised to address these points and below we provide responses to the individual questions raised by the referee. For each question the quoted referee text is in bold followed by our response.

1) Generating calibrated amounts of water vapor is a necessary step, but delivering them to an instrument at representative sampling conditions is another challenge that this manuscript didn't address. To this end, the proposed method still suffers from shortcomings of other low water vapor generation/calibration

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systems. For example, while generating 1.0 ppmv of water vapor from hydrogen/platinum is convincing, the resulting airstream is now at 200 C. What happens to that calibrated water vapor stream as it enters tubing and an instrument that are near room temperature (what is the temperature of the air upon reaching MBW)? Or, more relevant, how does this standard deliver at a temperatures/pressures closer to the measurement conditions of the atmosphere? While I convincingly believe that 1.0 ppmv of water vapor is produced immediately downstream of the catalyst based upon Figure 3, I'm not convinced that 1.0 ppmv will exist when reaching the sampling part of the instrument under more typical flight conditions (away from room temperature/pressure in the laboratory). Indeed, the calibration results in Fig. 3 show that the value of 0.55 ppmv is off by +/- 0.1 ppmv (or 20%). The authors attribute this to residual water vapor in the carrier flow, and while this seems reasonable, it would have been more convincing to see more data at sub ppmv ranges. Does a calculated flow of 0.2 ppmv also yield 0.1-0.3 ppmv as suggested, or is something limiting the system from going below 0.5 ppmv or there- about? No data is shown. While I realize atmospheric measurements don't reach this low of mole fraction, quantifying the offset is critical to making a believable calibration system.

The experiments reported here were conducted with all tubing at ambient temperature (21–24°C). This means that after leaving the catalyst the gas was cooled to room temperature before being measured by the MBW and we infer from Figure 3 that this did not result in losses of water prior to measurement. Text was added to lines 128-133 to explain this. The primary advantages that we find with this system over e.g. a liquid water saturator is that the catalyst is small and insensitive to ambient temperature, pressure and orientation. The catalyst can therefore be plumbed directly into the sampling port of e.g. an aircraft instrument, thereby adding a precisely known water vapor mixing ratio almost exactly at the instrument's sampling location. A statement to this effect was in the original manuscript and has been slightly expanded on (now lines 268-272). It is true that water may be lost on cold parts of an instrument after exiting

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the catalyst, but if the user of this system locates the catalyst in the appropriate place in their sampling inlet then these will be the same losses that ambient samples would encounter, and therefore are very relevant to the calibration. We therefore have confidence that this system can be used with relative ease to deliver known water vapor samples to an instrument at its sampling port.

Offset/zero issues:

As the reviewer discusses here and elsewhere in the review, quantifying an offset in any calibration system is critical. We neglected to state in the manuscript that the value of 0.1 ± 0.1 ppm of H₂O in the zero air that we used in our calculations was directly measured with the MBW, not inferred from other observed offsets. We expect that adding this detail to the text will address a number of the reviewer's concerns (now lines 115-116). Accurately measuring a value this low is challenging due to outgassing and the frost point instrument response characteristics at mixing ratios this low, and therefore assigning this uncertainty to the value was appropriate. Therefore any of the predicted water vapor concentrations that we would state would have a lower limit of uncertainty at ± 0.1 ppm. Text has been added to the manuscript discussing this (lines 119-121).

We chose to not pursue many measurements less than 1 ppmv for the following reasons. With water vapor, generating and measuring a true "zero" is challenging, and we believe somewhat unnecessary and less useful than a "near-zero". For example we could produce and measure extremely dry (< 10 ppb) zero air for a true instrument zero measurement but we find it just as (if not more) useful to produce an accurately known concentration that is only somewhat lower than what will be measured. Sampling H₂O standards into an instrument that are less than say 0.5 ppmv can result in long times required to obtain steady signals, resulting in relatively large uncertainties in the final signal value. In our experience it is much easier to measure the difference between air with 1.0 and 1.1 ppm than it is to measure the difference between 0.0 and 0.1 ppm. If one wishes to measure water vapor greater than say 2 ppmv, using

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a near-zero standard of 1.00 ± 0.05 would result in a much quicker and likely more accurate evaluation of the instrument background than if one were to try to dry out the instrument with completely dry air. As the reviewer notes concentrations < 1 ppmv are not encountered in the UT/LS and we are primarily interested in the ability to accurately produce calibration concentrations spanning the range of relevant atmospheric measurements. Instead we believe that an appropriate way to quantify the offset of our system is by using the intercept of the linear fit, which was -0.006 ppm. This gives us confidence that in producing calibration flows over the range of atmospheric interest, the standards are not being affected significantly by an offset. Discussion of these points has been added to the manuscript (lines 223-241).

I wonder how responsive the system is when using much slower flow rates (e.g. 100 sccm) at < 10 ppmv? Presumably the response time would be longer than 10 s and would be limited by sampling surfaces in the tubing or chilled mirror hygrometer. What would the response time be if the 851 ppmv H₂ standard were diluted (say, by 100:1) and flowed directly into the chilled mirror? As the authors know, very high flow rates (and/or high concentrations) can mask surface effects by quickly saturating adsorption sites. It would be interesting to know how the system responds at lower flow rates.

We have conducted experiments at various flow rates and generally observe as the reviewer suggests that lower flows are associated with longer equilibration times. For this reason we find using a higher flow rate to be an advantage since we are interested in eliminating as much as possible the impacts of surface effects on the measurements. The frost point instruments used as references here require flow rates of at least 500 sccm, so it was not possible to go as low as the 100 sccm as suggested.

Finally, to estimate background water effects, it would be helpful to see a step-wise challenge from 10 to effectively “zero” ppmv water vapor by turning off the Pt flow. Is this consistent with a 0.1 ppmv background claimed earlier?

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This is essentially how the 0.1 ppmv background in the zero air was determined. To quantify the water vapor in the zero air we valved off flow through the catalyst and flushed the zero air through the system until a steady signal was reached. This however did take hours of flushing to achieve, and part of this is due to the time constant of the frost point control algorithm, which is very slow at low concentrations.

These comments and suggestions above are to help understand the sampling artifacts in the experiments to gain more confidence in their “zero”.

We appreciate the reviewer’s concern for quantifying any offset in the calibration system. This was also a primary concern of ours in testing this technique. Because generating and measuring very near zero concentrations of water is very difficult, time consuming and not directly relevant to the atmosphere, as mentioned above we focused on the intercept of the linear fit of calculated vs measured H₂O as the best way to quantify an offset in the zero.

2. Introduction/title: Related to (1), I’m somewhat confused by the “in situ” claim. No data is shown for actually calibrating in-situ in flight. Instead, the setup is used for laboratory calibrations. While the technique has promise for in-flight calibrations, there are other issues that create problems (mentioned previously). A permeation tube or bubbler system in theory could also be “in situ”. While I agree that this is a portable and accurate system for generating known amounts of water vapor, I would recommend backing away from the in-situ claim. Yes, it may be helpful in the future for their CIMS instrument, but no data is presented to this end in the manuscript. Perhaps rephrasing the title to “. . .a compact method for generating accurate water vapor at > 1 ppmv” or something similar instead?

We agree that other techniques can in principle also be used in situ. We have rephrased the title and other points in the text such that it is now stated as being expected to be useful for in situ calibrations.

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3. Other minor points: p. 3086, top: how well-regulated was the pressure inside the tube via needle valve or critical orifice? What range of pressures were studied for the catalyst (you mention 2000 hPa later; may want to bracket the range used here)? The regulation doesn't appear to matter based upon later discussion, but it may be a metric to include anyway at this point (I wondered this initially).

Pressures between slightly above ambient (830 hPa in Boulder) and 2000 hPa were tried. We monitored the pressure during all experiments and it was maintained within 1

p. 3086, line 20: How were the 0.5 (and 0.1) ppmv background water vapor determined? MBW? The authors should explicitly state that the MBW-373LX is their water vapor reference standard.

Yes, the MBW was used to quantify all stated water vapor concentrations in the paper. We have added text (lines 115-116) to the manuscript explaining this.

p. 3086, line 23: What was the volume of the mixing manifold, and what were typical residence times for the flow rates that were used? What ratios of flows were used to make the lower mixing ratio concentrations (i.e. 2 sccm "dry" + 500 sccm hydro- genated)?

We have added some details of the tubing geometry, residence times and dilution factors to the text (lines 123-128, 193-194).

p. 3086, line 24: The gases were flowed through 0.5-1 m of tubing. What was the ambient temperature of gas when flowing directly (no dilution) to the chilled mirror? If it wasn't ambient, how did it change with flow rate/extent of dilution/longer tubing?

The temperature of the gas entering the MBW was always ambient. No attempt to control the temperature was made, and though the residence time here was short, the

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gas is expected to have equilibrated with the tubing walls outside and inside of the MBW. Text added to lines 128-133.

p. 3087, line 1-2: State explicitly that the FPH is calibrated by temperature/thermodynamic issues to ensure that no circular argument exists (i.e. if FPH were calibrated by MBW, and Pt method also calibrated by MBW, then FPH=Pt agreement wouldn't be surprising).

Thank you. We we have added text (lines 143-149) to explain this. The temperature and pressure calibrations of the MBW and FPH were indeed completely independent.

p. 3087, line 12: Clarification: a flow rate of ≤ 1000 sccm over the two pieces of mesh AND a total catalyst pressure of ≤ 2000 hPa at 200 C should provide total (within the uncertainty) conversion – i.e. if one were to use lower pressures or flow rates (or both), it should remain total conversion. If this is correct, please reword as appropriate. It provides a nice upper limit for full conversion given the various combinations of flow, pressure, and temperature. Also, since critical orifices require about a factor of two pressure differential, it helps constrain the upper pressure limit (within what has been observed) for using critical orifices with downstream pressures near ambient.

A decrease in the pressure with a constant mass flow rate would result in reducing the residence time in the catalyst and likely losing the full conversion. A reduction in pressure with a compensating reduction in flow rate would likely maintain the full conversion. We have added text (lines 179-185) discussing the pressure / flow relationship.

p. 3088, lines 1-5: if the stainless steel tube and Pt mesh worked so well as shown in Fig. 2, why were Pt tube and Pt mesh chosen here? My take home message from Fig. 2 is that one can use stainless steel tubing with mesh for effective conversion (and avoid Pt tubing). Just curious why one reverted to the Pt/Pt design – maybe because it worked just fine, but please clarify.

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The reviewer is correct that Fig 2 shows there is not a significant advantage to the Pt/Pt design over the SS/Pt design. The choice to use the Pt/Pt catalyst for the experiment to generate Figure 3 was somewhat arbitrary, and in the future we will likely use the SS/Pt more frequently due to the durability of stainless. This is explained on lines 191-193.

p. 3088, lines 1-5: How was it possible to reach sub 50 ppmv H₂O levels? 100 sccm of 851 ppmv H₂ = 851 ppmv H₂O, and this flow is then joined by 1400 sccm “dry” to yield a total flow of 1500 sccm. By my calculation, this would equate to a mixing ratio of 56.7 ppmv H₂O. What flows were needed to get 0.5 ppmv H₂O? My guess is that the 100 sccm flow was stepped from 1-100 sccm, but I don’t know.

This has been clarified in the text (lines 98-102, 189-194). A mixture of H₂ and ZA with a total flow rate of near 100 sccm was passed through the catalyst, and then this flow was further diluted with ZA. So for the lowest concentrations, an H₂ flow of 1.46 was mixed into a total flow of 2745 sccm. The total flow rate through the catalyst was maintained near 100 sccm, but this flow was a combination of ZA and H₂ that was varied.

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