

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

Anonymous Referee #1

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This manuscript describes a novel method to produce calibrated amounts of water vapor over a range of water vapor mole fractions, especially the 1-100+ ppmv range. Rollins et al. use calibrated amounts of hydrogen (a relatively easy gas to obtain in accurate concentrations) and convert the hydrogen at 100% efficiency to water vapor using a commonly-available Pt mesh catalyst. Hydrogen mixtures in air are much easier to prepare, store, and deliver than the corresponding water vapor mixtures in air, and thus one can buy accurate standards of hydrogen mixtures in air to yield calibrated water vapor measurements via the Pt conversion method. The manuscript presents another useful tool to cross-calibrate/intercompare with other methods in the laboratory for low water vapor mixing ratio measurements.

The calibration of water vapor sensors is critically important for atmospheric science.

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Water vapor exhibits its strongest radiative effects in the upper troposphere and lower stratosphere. At these altitudes, its mole fraction is often in the single ppm range in an environment of cold temperatures (~ 190 - 220 K) and low pressures (~ 50 - 200 hPa). Measurements from research grade water vapor instruments have disagreed with one another in this range, and a significant part of the problem is the difficulty in providing calibrated amounts of water under these conditions. For example, an unknown bias of even 0.5 ppmv (from outgassing of gas handling delivery system, residual water vapor in a flow, etc.) can be the difference between conventional and non-conventional ice nucleation microphysics at cold temperatures (< 200 K).

Overall, the manuscript is well-written, the experiments were convincingly performed, and I recommend publication. I do have some suggestions/clarifications below that may need to be elaborated upon, however.

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 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

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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 thereabout? 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.

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.

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?

These comments and suggestions above are to help understand the sampling artifacts in the experiments to gain more confidence in their "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?

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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).

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.

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 hydrogenated)?

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?

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).

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

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pressure differential, it helps constrain the upper pressure limit (within what has been observed) for using critical orifices with downstream pressures near ambient.

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 takehome 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.

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.

Overall, I find this to be an accurate (and compact) tool in providing a calibrated water vapor standard at ppmv levels to instruments, but I caution against any claims that this is “in-situ” when no evidence is presented. It would be slightly more helpful to have a better sense of their background via other experimental tests described above. I also am leery about calibration systems that are only demonstrated at room temperatures and pressures. Ultimately, calibrations need to be conducted at representative T, P, and q under which the measurements are also made. With that said, I believe this is an important method for the community as an orthogonal check against other systems/methods. I recommend publication after addressing these points.

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