

# Catalytic oxidation of H<sub>2</sub> on platinum: a robust method for generating low mixing ratio H<sub>2</sub>O standards

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**Abstract.** Standard reference samples of water vapor suitable for in situ calibration of atmospheric hygrometers are not currently widespread, leading to difficulties in unifying the calibrations of these hygrometers and potentially contributing to observed measurement discrepancies. We describe and evaluate a system for reliably and quantitatively converting mixtures of H<sub>2</sub> in air to H<sub>2</sub>O on a heated platinum surface, providing a compact, portable, adjustable source of water vapor. The technique is shown to be accurate and can be used to easily and reliably produce a wide range of water vapor concentrations ( $\approx 1$  ppm – 2 %) on demand. The result is a H<sub>2</sub>O standard that is expected to be suitable for in situ calibration of aircraft hygrometers, with an accuracy nearly that of the available H<sub>2</sub> standards ( $\approx \pm 2$  %).

## 1 Introduction

Water vapor mixing ratios reach the low parts per million (ppm) range in Earth's upper troposphere and lower stratosphere (UT/LS), with the lowest values found near the tropical tropopause and in the Antarctic stratosphere. UT/LS water vapor is of particular interest due to its role in surface climate forcing (Solomon et al., 2010). The calibrations of instruments that measure low concentrations of water vapor are tied to prior thermodynamic or spectroscopic knowledge of water. For example, the longest continual record of UT/LS water vapor has been made with chilled mirror (frost point) hygrometers, which measure the temperature at which ice is

in equilibrium with ambient water vapor (e.g. Hurst et al., 2011). The accuracy of these hygrometers relies on the calibration of the thermistor used to measure the mirror temperature, and the accuracy with which this calibration quantifies the ice temperature (e.g. Vömel et al., 2007). Measurements of water vapor traceable to H<sub>2</sub>O spectroscopic transitions include open and closed path absorption spectrometers (e.g. May, 1998), and ground or space-based remote sensing instrumentation (e.g. Read et al., 2007; McDermid et al., 2011). H<sub>2</sub>O permeation sources that emit water at a known rate and commercial or custom flow saturation systems are frequently used to calibrate aircraft instruments in the laboratory before and after flight (Zöger et al., 1999).

A large suite of in situ and remote sensing instruments that are calibrated in these various ways have been used to measure UT/LS water vapor mixing ratios. Coincident comparisons of these measurements have shown that significant systematic differences typically occur at mixing ratios below 10 ppm (Oltmans and Rosenlof, 2000; Peter et al., 2006; Vömel et al., 2007; Weinstock et al., 2009). In contrast, a recent laboratory intercomparison (Fahey et al., 2009) demonstrated substantially better agreement, suggesting that the observed in situ discrepancies may be due to differences between laboratory and in situ operation on moving platforms. Resolving these discrepancies can be aided by the development of more frequently used in situ calibration systems.

While in situ calibrations of airborne instruments have been performed via addition of H<sub>2</sub>O into the instrument inlet while deployed on an aircraft (e.g. Kelly et al., 1989), this procedure is atypical. Part of the challenge in calibrating this way is in producing a portable source of water vapor with a known and controllable concentration, and with a flow that is scalable to instrument sample flow rates. We report the



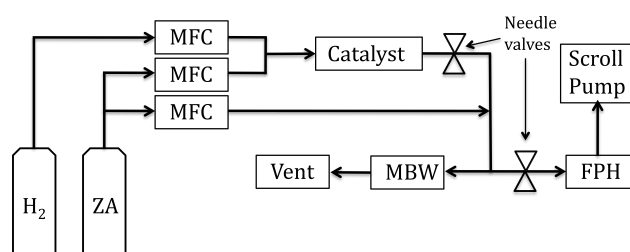
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design and evaluation of a compact, portable source of water vapor that can reliably provide known mixing ratios over a wide dynamic range, and which, based on our laboratory evaluation, appears suitable for in situ use aboard aircraft. The method utilizes the catalytic oxidation of H<sub>2</sub> on a platinum (Pt) surface. This reaction has been the focus of a number of experimental and theoretical studies (e.g. Völkening et al., 1999, and references therein) and has been used in at least one other instance for generating water vapor standards (Mackrodt and Fernandes, 2001). Here we report quantitative conversion of H<sub>2</sub> to H<sub>2</sub>O within the accuracy of the available H<sub>2</sub> standards, and demonstrate the ability to produce H<sub>2</sub>O concentrations down to  $\approx 0.5$  ppm in a flow of 1500 standard cubic centimeters per minute (sccm).

## 2 Experiment

Catalytic conversion flow tubes were constructed both of 0.216 cm i.d. Pt tubing (0.995, Refining Systems, Inc., Las Vegas, NV, USA) and 100 mesh Pt gauze (0.999, Sigma-Aldrich part no. 298093) rolled up and inserted inside either the Pt tube or a 0.493 cm i.d. 316 stainless steel (SS) tube. The Pt tube has a surface area to volume ratio of  $19 \text{ cm}^2 \text{ cm}^{-3}$ , while the Pt gauze rolled up inside a tube has an estimated surface area to volume ratio of  $63 \text{ cm}^2 \text{ cm}^{-3}$  ( $\approx 52 \text{ cm}^2$  of Pt surface area for one  $5 \times 5 \text{ cm}$  gauze). Both Pt and SS tubes used were 14 cm long and were mounted in solid copper blocks configured with cartridge heaters. The temperature of the catalysts was measured with a type-K thermocouple inserted into a small hole drilled in the heater blocks. A PID (proportional/integral/derivative) temperature controller was used to maintain the temperature of the catalysts to  $\pm 0.5^\circ \text{C}$ . A needle valve or critical orifice was used at the outlet of the tubes to maintain the gas pressure above ambient inside the catalyst tube in some of the experiments. The pressure in the catalyst was varied from slightly above ambient (830 hPa) to 2000 hPa and was monitored with a pressure transducer (Trans-Metrics) and observed to be stable to within  $\pm 1\%$  during the experiments.

Several H<sub>2</sub> standards were used for the experiments. Mixtures of H<sub>2</sub> in dry air with concentrations ranging from 201 ppm to 2.00 % were obtained from Air Liquide (Plumsteadville, PA) with analytical accuracies of  $\pm 5\%$ . Additionally, a cylinder with  $850.9 \pm 6.4 \text{ ppm}$  ( $\pm 0.75\%$ ) H<sub>2</sub> was obtained from the NOAA/ESRL Global Monitoring Division that was produced using gravimetric static dilution (Novelli et al., 1991; Hall et al., 2007). In some experiments the H<sub>2</sub> standards were passed directly through a catalyst and the resulting H<sub>2</sub>O concentration was measured without dilution. In experiments requiring variable concentrations, a series of mass flow controllers (MFC, Tylan 260) were used to produce dynamic dilutions of H<sub>2</sub> in additional flows of zero air (Air Liquide). A combined total flow of H<sub>2</sub>/air and zero air near 100 sccm was passed through the catalyst and then



**Fig. 1.** Diagram of the components used for the dynamic dilution experiments. Two mass flow controllers (MFC) generated mixtures of H<sub>2</sub> in zero air (ZA), which passed through a Pt catalyst and needle valve or critical orifice before mixing with additional zero air. The resulting H<sub>2</sub>O was measured with an MBW 373LX frost point hygrometer operated at ambient pressure, and a custom frost point hygrometer backed by a scroll pump and operated at approximately 100 hPa.

mixed with more zero air to further dilute the H<sub>2</sub>O produced in the catalyst. Figure 1 shows the components and experimental configuration used in the dilution experiments. Multiple DryCal flow meters (Bios International Corp.) were used to calibrate the flow controllers used in all experiments. The DryCal flow meters are a primary standard for volumetric flow rate with a stated accuracy of  $\pm 1\%$ . Here we calibrated the MFCs with 4 different DryCal units and observed agreement to within  $\pm 1\%$ . The volumetric flow rate measurements were converted to mass flow using the temperature measured by two type-K thermocouples (Fluke,  $\pm 0.2\%$  accuracy), and pressure measured using two vibrating cylinder pressure sensors (Weston Aerospace,  $\pm 0.01\%$  accuracy). However, the mixing ratio calculations stated here are unaffected by the accuracy of temperature and pressure measurements since these factors cancel when calculating the volumetric mixing ratio.

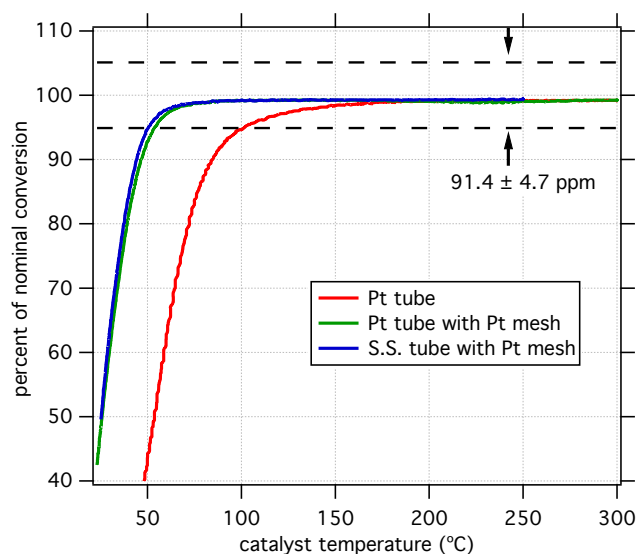
The H<sub>2</sub>O in the zero air tanks used for the experiments was quantified using an MBW 373LX frost point hygrometer (MBW Calibration Ltd., Switzerland). These tanks were observed to consistently contain less than 0.5 ppm H<sub>2</sub>O. A molecular sieve moisture trap (Agilent Technologies) was used to further reduce the H<sub>2</sub>O concentration in the zero air to  $0.1 \pm 0.1 \text{ ppm}$ . The large uncertainty stated here in the H<sub>2</sub>O content of the zero air results from the extremely long time constant (hours) associated with measuring mixing ratios this low. The time constant depends on the continued outgassing of water from internal surfaces of the MBW and the highly damped nature of its control algorithm. In all experiments, gases were mixed in a manifold of 0.175 cm i.d. electropolished stainless steel tubing (Winter Technologies), with a total internal volume of approximately  $0.7 \text{ cm}^3$ . The mixed gases were transferred to the MBW through 0.5–1 m of 0.635 cm o.d. Synflex tubing (Type 1300, Eaton Corp) to measure the water vapor mixing ratio. Total residence time in the mixing and transfer tubing was approximately 1 s. None of the tubing other than the catalyst was actively heated,

allowing the gas to reach room temperature (21–24 °C) prior to entering the MBW. As seen in the results, the cooling of the catalyst output did not result in a measureable loss of H<sub>2</sub>O on the tubing, as was our expectation due to the extremely sub-saturated condition of the flow.

The MBW instrument used for all reported H<sub>2</sub>O measurements is a NIST traceable standard for water vapor measurement. It has an accuracy of  $\pm 0.1$  °C in the frost point, which at 830 hPa (typical ambient/experimental pressure in Boulder, CO) is  $\pm 1.6$  % of a 1-ppm mixing ratio. In some experiments, an additional custom frost point hygrometer (FPH) instrument (Thornberry et al., 2011) was used to corroborate the MBW measurements. For these experiments, a tee was used to sample in parallel 200–400 sccm of the total flow into the FPH through a critical orifice. The MBW and FPH were observed to agree at all concentrations to within 1–2 %. The calibration of the FPH is independent of that of the MBW. Water vapor measured with the FPH is calculated from: (1) the frost point which is determined by thermistors calibrated to a NIST traceable temperature standard, and (2) the pressure which was also determined by the Weston pressure standard. The Goff-Gratch equation for the vapor pressure of water over hexagonal ice is used to calculate the water vapor mixing ratio from the measured temperature and total pressure. The frost point instruments were chosen for this study due to the NIST traceable nature and reliability of the measurement. While significant discrepancies have been noted between measurements made by various water vapor instruments in the atmosphere, in laboratory settings these discrepancies are not typically observed (Fahey et al., 2009). Hence, we expect that our results were not significantly affected by the choice of water vapor measurement.

### 3 Results

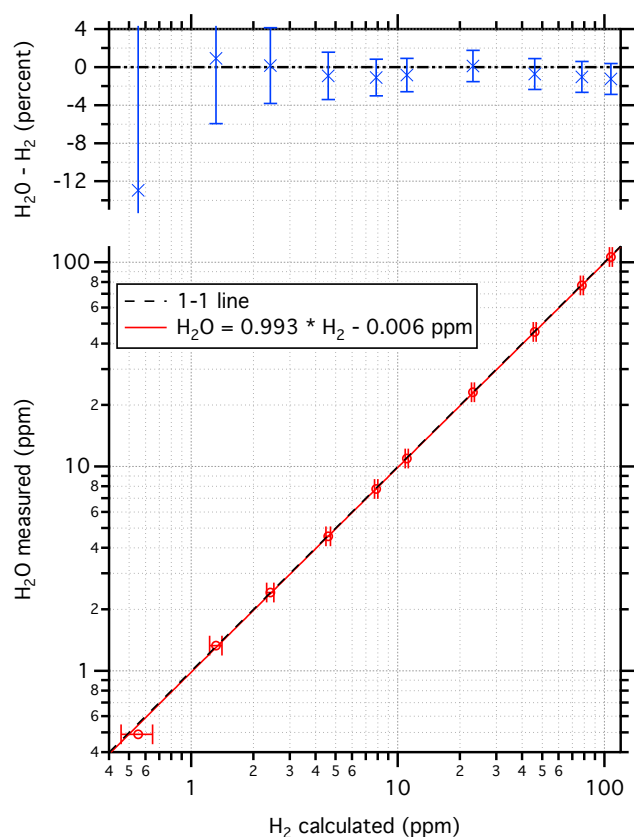
An initial set of experiments was performed to determine the temperature, flow rate and pressure dependences of the conversion efficiency. For the temperature experiments, a constant H<sub>2</sub> concentration ( $91.4 \pm 4.7$  ppm) was sampled through the catalyst while its temperature was scanned at 100–150 °C h<sup>-1</sup>. Figure 2 shows the observed temperature dependence from individual experiments for the 0.493-cm stainless steel tube with Pt mesh, the bare 0.216 cm Pt tube, and the Pt tube with Pt mesh. Here all catalysts were operated at near ambient pressure and 100 sccm total flow. The catalyst temperature was scanned both up and down in temperature, and hysteresis on the order of 5–10 °C was observed, likely due to slight differences between the temperature of the Pt surface and the temperature measured on the heater block. In all cases 200 °C was observed to be sufficient for full conversion with the H<sub>2</sub>O concentration observed at this temperature equal to the mixing ratio of the H<sub>2</sub> within the uncertainty of the mixture ( $\pm 5.1$  %).



**Fig. 2.** Temperature dependence of conversion of H<sub>2</sub> to H<sub>2</sub>O for 3 catalyst designs. Water vapor was measured with an MBW 373LX hygrometer. For this experiment an H<sub>2</sub> cylinder with  $91.4 \pm 4.7$  ppm was used. Nominal conversion is calculated as measured mixing ratio/ $91.4 \times 100$  %, and the range of observed conversion that would be within the uncertainty of the H<sub>2</sub> cylinder is indicated.

The flow rate dependence of the conversion efficiency was determined by varying the flow rate of H<sub>2</sub> through the catalyst and measuring the resulting H<sub>2</sub>O without dilution. Using the catalysts with a single piece of 5 cm × 5 cm mesh at 200 °C, greater than 99 % conversion was observed for flow rates up to 500 sccm with 503 ppm and 2.00 % H<sub>2</sub>. An additional catalyst with two pieces of this mesh was used to achieve greater than 99 % conversion at flow rates up to 1000 sccm. In a number of experiments the internal pressure of the catalyst tube was increased from ambient up to  $\approx 2000$  hPa. Typically, at lower temperatures ( $< 100$  °C) where H<sub>2</sub> was not fully converted to H<sub>2</sub>O, a small increase (1–2 %) in the conversion efficiency was observed upon increasing the catalyst operating pressure. Increasing the pressure at a constant mass flow increases the residence time in the catalyst, thus improving the conversion efficiency. It is possible that significantly higher flows may be achieved with much higher pressures, but this was not tested here and other limiting factors such as H<sub>2</sub> diffusion to the Pt surfaces and availability of active sites on the Pt may become limiting.

To demonstrate the capability of the Pt catalyst for producing a series of low H<sub>2</sub>O mixing ratios for calibration, we used the Pt tube containing Pt mesh at 200 °C and a total flow rate (H<sub>2</sub> in ZA + additional ZA, mixed with two MFCs) of 100 sccm through the catalyst to produce steps of H<sub>2</sub>O from 0.55–107 ppm in a total flow of 1500–2475 sccm. The Pt-tube was used instead of a stainless tube out of convenience and because the results from the temperature tests (Fig. 2) did not significantly differ between designs. For this experiment



**Fig. 3.** Observed water vapor mixing ratios produced from a dynamic dilution of an H<sub>2</sub>/zero air mixture. Error bars represent the  $2\sigma$  uncertainty in expected H<sub>2</sub>O due to accuracy of the H<sub>2</sub> bottle ( $\pm 0.75\%$ ), 3 flow controllers (1 % each) and H<sub>2</sub>O in zero air used for dilution ( $0.1 \pm 0.1$  ppm). Top panel: Vertical range is selected to clearly show the uncertainty range for most of the points. The lowest concentration point (0.55 ppm) has an uncertainty of  $\pm 20\%$  which exceeds the range shown. Water vapor was measured with an MBW 373LX hygrometer.

the  $850.9 \pm 6.4$  ppm H<sub>2</sub> reference standard was used with total dilution factors ranging from 7.93 to 1880. The time typically required to achieve a steady measurement of H<sub>2</sub>O after changing the H<sub>2</sub> flow was 10 s. The time constant associated with acquiring a stable signal was determined to be mostly due to the frost point instruments, not the H<sub>2</sub>O source. This was clear from the different response times of the different frost point instruments. At sub-5 ppmv concentrations the MBW would require extended time periods to achieve a stable signal (minutes) while the FPH responded within seconds. This may be due almost entirely to the PID control algorithm, which in the FPH is designed for quick response to changes, and in the MBW is designed for stability.

We show the results of the accuracy test in Fig. 3. Here the measured H<sub>2</sub>O mixing ratio is plotted against the mixing ratio calculated assuming 100 % conversion of the H<sub>2</sub>. Error bars show the combined uncertainty ( $2\sigma$ ) associated with the

H<sub>2</sub> mixture, residual H<sub>2</sub>O in the zero air ( $0.1 \pm 0.1$  ppm), and flow controller accuracy. Uncertainties in the MBW measurements have been omitted for clarity, but range from 1.7 % of the mixing ratio at 0.55 ppm to 1.2 % of the mixing ratio at 107 ppm. For all mixing ratios, the measurements agree with the predicted H<sub>2</sub>O within the combined uncertainties (typically  $\pm 2$ –3 %). At low mixing ratios the total uncertainty is dominated by the uncertainty in the residual H<sub>2</sub>O in the zero air. At high mixing ratios the uncertainty is mainly that of the mass flow controllers. The excellent linear fit to the data shown in Fig. 3 (slope = 0.993, offset =  $-0.006$  ppm,  $R^2 = 1.000$ ) confirms both the near unity conversion of H<sub>2</sub> to H<sub>2</sub>O in our system, and its ability to produce a wide range of H<sub>2</sub>O sample mixing ratios with high absolute accuracy. The near-zero intercept of the fit ( $-0.006$  ppm) confirms that no unexpected offset between the calculated and produced water vapor concentrations exists with this system, provided there is an accurate assessment of the H<sub>2</sub>O content of the zero air.

We have observed throughout these experiments that quantifying mixing ratios lower than a few tenths of a ppm in an attempt to establish an instrumental “zero” for a hygrometer intended for atmospheric measurement is both challenging and time consuming, and likely results in an increased uncertainty in the measurement due to the long equilibration times required for such dry flows. For example, measuring the difference between 1.0 ppm and 1.1 ppm can be done much more accurately and quickly than measuring the difference between 0.1 and 0.2. This is due both to out-gassing, and to the fact that a mixing ratio of 0.1 ppm even at 1013 hPa is a frost point of  $\approx -90^\circ\text{C}$  which is at or near the lower limit for frost point instruments. Therefore, we have found it more useful to evaluate potential artifacts in our measurement systems, and in the calibration system, by producing and measuring atmospherically relevant concentrations, rather than attempting to measure extremely low amounts that do not occur in the atmosphere. In the present study the lowest mixing ratio that we report is 0.55 ppm which is indeed lower than will be encountered in the UT/LS. Based on this work presented here, we recommend that the most reliable method to calibrate UT/LS water vapor measurement systems is to produce calibration mixing ratios that span a range that has a minimum value that is only somewhat lower than any value that will be measured, and a similarly chosen maximum value.

## 4 Conclusions

The ability to quantitatively and reliably convert H<sub>2</sub> standards to H<sub>2</sub>O represents a step forward in the available options to calibrate hygrometers due to the ease of producing a large dynamic range of H<sub>2</sub>O over a short period of time, as well as having absolute accuracy based on an independent set of H<sub>2</sub> primary standards. While this method is applicable to use in the laboratory, we expect it will be particularly

useful for in situ calibration of research hygrometers integrated onboard aircraft where multiple calibration concentrations are desired, and where the environment (e.g. temperature, pressure, vibration) in which the calibration system is contained may be highly variable and difficult to control. As is shown in Fig. 1 the design is simple and robust. This system requires no liquid handling, whereas the implementation of a liquid H<sub>2</sub>O saturator such as is typically used in laboratory calibrations would be significantly more complicated in a moving, unpressurized and unheated aircraft environment. The results displayed in Fig. 3 were obtained using a critical orifice at the catalyst outlet as shown in Fig. 3, rendering the system insensitive to the catalyst outlet pressure or similarly the target instrument's inlet pressure which may vary during a flight. Assuming that the performance of the flow controllers used are unaffected by the aircraft environment, the accuracy of the system will also be unaffected. Finally, the observed response time of the H<sub>2</sub>O output to changes in the input flows was consistently less than 10 s (limited to the MBW and FPH response time). Therefore, a number of H<sub>2</sub>O concentrations spanning a large dynamic range can be sampled into an instrument inlet in the course of minutes.

We have used the Pt mesh versions of catalysts described here continuously for months of daily use in our laboratory without any observed decrease in catalytic efficiency. Unlike H<sub>2</sub>O, H<sub>2</sub> does not have an affinity for stainless steel or Teflon tubing materials. It can easily be diluted to the desired concentration using flow controllers and converted to H<sub>2</sub>O at an instrument's inlet by locating the catalyst immediately prior to the sampling port to minimize effects of H<sub>2</sub>O loss or enhancement from the wetted surfaces. The catalyst system we have described here is compact ( $\approx 2\text{ cm} \times 3\text{ cm} \times 15\text{ cm}$  excluding the gas cylinders and flow controllers) and requires little power (10 W with  $\approx 5\text{ mm}$  thick ceramic foam insulation around the copper heater block). The specific design reported here was built to generate concentrations of  $\approx 1\text{--}300\text{ ppm}$  in flows of  $1500\text{--}2000\text{ sccm}$ . While practical flow and detection axis design limitations constrain which of the existing water vapor instruments could easily implement the system described here, instruments do exist to which it is immediately applicable due to their sample flow rates. Larger total flow rates can be accommodated by either converting a higher concentration of H<sub>2</sub> prior to dilution, or by increasing the total Pt surface area by using a larger tube to accommodate higher flow rates through the catalyst. Thus, instruments requiring much different flow rates for calibration may be calibrated using the same primary reference.

In this work we have demonstrated a method that can be used to provide low concentration ( $1\text{--}10\text{ ppm}$ ) water vapor calibration samples, with accuracies better than  $\pm 5\%$ . As previous aircraft campaigns have demonstrated instrumental differences in this mixing ratio range in large excess of this level of accuracy, the system described here is relevant and should be useful towards resolving these discrepancies.

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## References

- Fahey, D. W., Gao, R.-S., and Möhler, O.: Summary of the AquaVIT Water Vapor Intercomparison: Static Experiments, [https://aquavit.icg.kfa-juelich.de/WhitePaper/AquaVITWhitePaper\\_Final\\_23Oct2009\\_22MB.pdf](https://aquavit.icg.kfa-juelich.de/WhitePaper/AquaVITWhitePaper_Final_23Oct2009_22MB.pdf), 2009.
- Hall, B. D., Dutton, G. S., and Elkins, J. W.: The NOAA nitrous oxide standard scale for atmospheric observations, *J. Geophys. Res.*, 112, D09305, doi:10.1029/2006JD007954, 2007.
- Hurst, D. F., Oltmans, S. J., Vömel, H., Rosenlof, K. H., Davis, S. M., Ray, E. A., Hall, E. G., and Jordan, A. F.: Stratospheric water vapor trends over Boulder, Colorado: Analysis of the 30 year Boulder record, *J. Geophys. Res.*, 116, D02306, doi:10.1029/2010JD015065, 2011.
- Kelly, K. K., Tuck, A. F., Murphy, D. M., Proffitt, M. H., Fahey, D. W., Jones, R. L., McKenna, D. S., Loewenstein, M., Podolske, J. R., Strahan, S. E., Ferry, G. V., Chan, K. R., Vedder, J. F., Gregory, G. L., Hynes, W. D., McCormick, M. P., Browell, E. V., and Heidt, L. E.: Dehydration in the lower Antarctic stratosphere during late winter and early spring, 1987, *J. Geophys. Res.*, 109, 11317–11357, 1989.
- Mackrodt, T. and Fernández, F.: The PTB Coulometric Humidity Generator as primary standard for trace humidity measurements in gases, *Proc. TEMPMEKO 2001*, 589–596, 2001.
- May, R. D.: Open-path, near-infrared tunable diode laser spectrometer for atmospheric measurements of H<sub>2</sub>O, *J. Geophys. Res.*, 103, 19161–19172, 1998.
- McDermid, I. S., Leblanc, T., and Walsh, T. D.: Ground-based water vapor Raman lidar measurements up to the upper troposphere and lower stratosphere – Part 1: Instrument development, optimization, and validation, *Atmos. Meas. Tech. Discuss.*, 4, 5079–5109, doi:10.5194/amtd-4-5079-2011, 2011.
- Novelli, P. C., Elkins, J. W., and Steele, L. P.: The development and evaluation of a gravimetric reference scale for measurements of atmospheric carbon monoxide, *J. Geophys. Res.*, 104, 13109–13121, 1991.
- Oltmans, S. and Rosenlof, K.: Chapter 2: Data Quality, in: *SPARC Assessment of Upper Tropospheric and Stratospheric Water Vapour*, 2000.
- Peter, T., Marcolli, C., Spichtenger, P., Corti, T., Baker, M. B., and Koop, T.: When dry air is too humid, *Science*, 314, 1399–1402, doi:10.1126/science.1135199, 2006.
- Read, W. G., Lambert, A., Bacmeister, J., Cofield, R. E., Christensen, L. E., Cuddy, D. T., Daffer, W. H., Drouin, B. J., Fetzner, E., Froidevaux, L., Fuller, R., Herman, R., Jarnot, R. F., Jiang, J. H., Jiang, Y. B., Kelly, K., Knosp, B. W., Kovalenko, L. J., Livesey, N. J., Liu, H.-C., Manney, G. L., Pickett, H. M., Pumphrey, H. C., Rosenlof, K. H., Sabouchi, X., Santee, M. L., Schwartz, M. J., Snyder, W. V., Stek, P. C., Su, H., Takacs, L. L., Thurstans, R. P., Vömel, H., Wagner, P. A., Waters, J. W., Webster, C. R., Weinstock, E. M., and Wu, D. L.: Aura Microwave Limb Sounder upper tropospheric and lower stratospheric H<sub>2</sub>O and relative humidity with respect to ice validation, *J. Geophys. Res.*, 112, D24S35, doi:10.1029/2007JD008752, 2007.
- Solomon, S., Rosenlof, K. H., Portmann, R. W., Daniel, J. S., Davis, S. M., Sanford, T. J., and Plattner, F.-K.: Contributions of Stratospheric Water Vapor to Decadal Changes

- in the Rate of Global Warming, *Science*, 327, 1219–1223, doi:10.1126/science.1182488, 2010.
- Thornberry, T., Gierczak, T., Gao, R. S., Vömel, H., Watts, L. A., Burkholder, J. B., and Fahey, D. W.: Laboratory evaluation of the effect of nitric acid uptake on frost point hygrometer performance, *Atmos. Meas. Tech.*, 4, 289–296, doi:10.5194/amt-4-289-2011, 2011.
- Völkening, S., Bedürftig, K., Jacobi, K., Wintterlin, J., and Ertl, G.: Dual-Path Mechanism for Catalytic Oxidation of Hydrogen on Platinum Surfaces, *Phys. Rev. Lett.*, 83, 2672–2675, doi:10.5194/amt-4-289-2011, 1999.
- Vömel, H., David, D. E., and Smith, K.: Accuracy of tropospheric and stratospheric water vapor measurements by the cryogenic frost point hygrometer: Instrumental details and observations, *J. Geophys. Res.*, 112, D08305, doi:10.1029/2006JD007224, 2007.
- Weinstock, E. M., Smith, J. B., Sayres, D. S., Pittman, J. V., Spackman, J. R., Hints, E. J., Hanisco, T. F., Moyer, E. J., St. Clair, J. M., Sargent, M. R., and Anderson, J. G.: Validation of the Harvard Lyman- in situ water vapor instrument: Implications for the mechanisms that control stratospheric water vapor, *J. Geophys. Res.*, 114, D23301, doi:10.1029/2009JD012427, 2009.
- Zöger, M., Afchine, A., Eicke, N., Gerhards, M.-T., Klein, E., McKenna, D. S., Mörschel, U., Schmidt, U., Tan, V., Tuitjer, F., Woyke, T., and Schiller, C.: Fast in situ stratospheric hygrometers: A new family of balloon-borne and airborne Lyman  $\alpha$  photofragment fluorescence hygrometers, *J. Geophys. Res.*, 104, 1807–1816, 1999.