**Atmospheric
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Catalytic oxidation of H_2 on platinum: a method for in situ calibration of hygrometers

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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 measurement discrepancies. We describe and evaluate a system for reliably and quantitatively converting mixtures of H$_2$ in air to H$_2$O on a heated platinum (Pt) surface, providing a compact, portable, adjustable source of water vapor. The technique is shown to be accurate and can be used to easily and predictably produce a wide range of water vapor concentrations (≈ 1 ppm-2 %) on demand. The result is a H$_2$O standard that is suitable for in situ calibration of hygrometers, with an accuracy nearly that of the available H$_2$ 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 being found near the tropical tropopause. UT/LS water vapor is of particular interest due to its role in surface climate forcing (Solomon et al., 2010). The calibration of instruments that measure low concentrations of water vapor are tied either to prior thermodynamic or spectroscopic knowledge of water. For example the longest standing record of UT/LS water vapor has been made with chilled mirror (frostpoint) hygrometers, which measure the temperature at which ice is in equilibrium with ambient water vapor (Hurst et al., 2011). The accuracy of these hygrometers relies on the calibration of the measurement of the ice temperature (e.g., Vömel et al., 2007). Calibrations of water vapor measurements traceable to H$_2$O spectral transitions include open and closed path absorption spectrometers (e.g. May, 1998), and satellite measurements (Read et al., 2007). Calibrated H$_2$O permeation sources or water bubblers in which saturation of the vapor is assumed are frequently used to calibrate aircraft instruments in the lab (Zöger et al., 1999). A large suite of remote sensing and in situ instruments have measured UT/LS

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water vapor mixing ratios, and comparisons of these have shown that significant systematic discrepancies exist below 10 ppm (Oltmans and Rosenlof, 2000; Peter et al., 2006; Vömel et al., 2007; Weinstock et al., 2009). A recent laboratory intercomparison (Fahey et al., 2009) demonstrated better agreement, suggesting that the discrepancies may be due to the differences between laboratory and in situ operation. 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 a standard 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 design and evaluation of a small, portable source of water vapor that can reliably provide known mixing ratios over a wide dynamic range. The method utilizes the catalytic oxidation of H$_2$ on a platinum surface. This reaction has been the focus of many experimental and theoretical studies (e.g. Völkening et al., 1999, and references therein) and has been used in at least one other method for generating water vapor standards (Mackrodt and Fernandes, 2001). Here we report quantitative conversion of H$_2$ to H$_2$O within the accuracy of the available H$_2$ standards, and demonstrate the ability to produce H$_2$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 solid 99.5 % Pt tubing (0.216 cm i.d.), and 5 cm × 5 cm, 100 mesh Pt gauze (Aldrich) rolled up and inserted inside of the Pt tube (Refining Systems, Inc., Las Vegas, NV, USA), or a 0.635 cm o.d. stainless steel (316) tube. The Pt tube has a surface area to volume ratio of 19 cm^2 cm^{-3}, while the Pt gauze rolled up inside a tube has an estimated surface area

to volume ratio of 63 cm^2 cm^{-3} ($\approx$52 cm^2 of Pt surface area for one 5 cm × 5 cm gauze). The tubes 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 temperature controller was used to maintain the temperature of the catalysts to ±0.5°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.

Several H$_2$ standards were used for the experiments. Mixtures of H$_2$ in dry air with concentrations ranging from 201 ppm to 2.00 % were obtained from Air Liquide (Plumsteadville, PA) with analytical accuracies of ±5 %. Additionally, a cylinder with 850.9 ± 6.4 ppm (±0.75 %) H$_2$ 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$_2$ standards were passed directly through a catalyst and the resulting H$_2$O concentration was measured without dilution. In experiments requiring variable concentrations, a series of mass flow controllers (Tylan 260) were used to produce dynamic dilutions of H$_2$ in zero air (Air Liquide) and additional zero air was used to further dilute the H$_2$O produced in the catalyst. Figure 1 shows the components and configuration used in the dilution experiments. Multiple DryCal flow meters (Bios International Corp.) were used to calibrate the flow controllers used in all experiments to ±1 % accuracy. The zero air tanks used for the experiments were observed to consistently contain less than 0.5 ppm H$_2$O and a molecular sieve moisture trap (Agilent Technologies) was used to further reduce the H$_2$O concentration in the zero air to 0.1 ± 0.1 ppm. In all experiments, gases were mixed in a stainless steel manifold and 0.5–1 m of 0.635 o.d. Synflex hose (Eaton Corp.) was used to transfer the water vapor flow to an MBW 373LX frostpoint hygrometer (MBW Calibration Ltd., Switzerland) to measure the water mixing ratio. The MBW accuracy is ±0.1 °C in the frostpoint, which at 830 hPa (typical ambient/experimental pressure in Boulder, CO) is ±1.6 % of the mixing ratio at 1 ppm and improves at higher mixing ratios. In some experiments, an additional custom frost point hygrometer (FPH) instrument

(Thornberry et al., 2011) was used to corroborate the MBW measurements. In this case 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 found to agree at all concentrations to within 1–2 %.

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$_2$ concentration (91.4 ± 4.7 ppm) was sampled through the catalyst while its temperature was scanned at 100–$150\,°C\,h^{-1}$. Figure 2 shows the observed temperature dependence from individual experiments for the 0.635 cm stainless steel tube with Pt mesh, the bare 0.318 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$_2$O concentration observed at this temperature equal to the mixing ratio of the H$_2$ within the uncertainty of the mixture (± 5.1 %).

The flow rate dependence of the conversion efficiency was determined by varying the flow rate of H$_2$ through the catalyst and measuring H$_2$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$_2$. 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 ≈ 2000 hPa. Typically at lower temperatures ($<100\,°C$) where H$_2$ was not fully converted to H$_2$O, a small increase (1–2 %) in the conversion efficiency was observed at increased catalyst operating pressure.

To demonstrate the use of the Pt catalyst for producing a series of low H_2O mixing ratios for calibration, we used the Pt tube with Pt mesh design at 200 °C and a flow rate of 100 sccm through the catalyst to produce steps of H_2O from 0.55–107 ppm in a total flow of 1500 sccm. For this experiment the 850.9 ± 6.4 ppm H_2 reference standard was used. The time typically required to achieve a steady measurement of H_2O after changing the H_2 flow was 10 s and appeared to be limited by the frost point instrument's response time. Figure 3 shows the measured H_2O plotted against the H_2O calculated assuming 100 % conversion of the H_2. Error bars show the combined uncertainty (2σ) associated with the H_2 mixture, H_2O in the zero air, and flow controller accuracy. For all concentrations the measurements agree with the predicted H_2O within the combined uncertainties (typically ±2–3 %). At low mixing ratios the uncertainty is dominated by the background H_2O 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) further confirms both the near unit conversion of H_2 to H_2O in our system, and its ability to produce a wide range of H_2O sample mixing ratios with high absolute accuracy.

4 Conclusions

The ability to quantitatively and reliably convert H_2 standards to H_2O represents a step forward in the available options to calibrate hygrometers due to the ease of producing a large dynamic range of H_2O over a short period of time, as well as having absolute accuracy based on an independent set of H_2 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 on board aircraft where multiple calibration concentrations are desired, and 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 implimentation of a liquid H_2O saturator such as is typically

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used in laboratory calibrations would be significantly more complicated in a moving, unpressurezed and unheated aircraft environment. The results displayed in Fig. 3 were obtained using a critical orifice at the catalyst outlet as shown in Fig. 1, 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$_2$O output to changes in the input flows was consistantly less than 10 s (limited to the MBW and FPH response time) at all H$_2$O concentrations. Therefore, a number of H$_2$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 lab without any observed decrease in catalytic efficiency. Unlike H$_2$O, H$_2$ 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$_2$O immediately prior to sampling to minimize effects of H$_2$O loss or enhancement from the wetted surfaces. The catalyst system we have described here is compact ($\approx$2 cm $\times$ 3 cm $\times$ 15 cm excluding the gas cylinders and flow controllers) and requires little power (10 W with $\approx$5 mm thick ceramic foam insulation around the copper heater block). The specific design reported here was built to generate concentrations of $\approx$1–300 ppm in flows of 1500–2000 sccm. While practical flow and detection axis design limitations constrain which of the existing water vapor instruments could easily impliment the system described here, instruments do exist to which it is immediately applicable due to their sample flow rates. Larger total flow rates can be accommodated by either converting a higher concentration of H$_2$ 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 (1–10 ppm) water vapor calibration samples, with accuracies better than ±5 %. As previous aircraft campaigns have demonstrated instrumental differences in this concentration range in large excess of this level of accuracy, the system described here is relevant to resolving these discrepancies.

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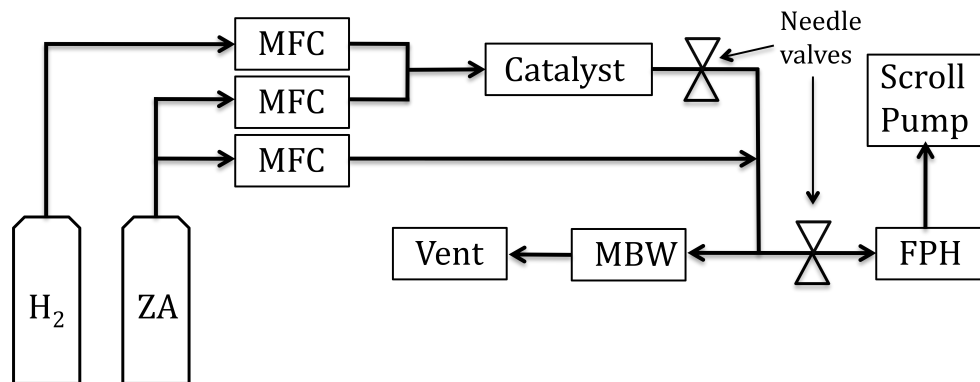
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Fig. 1. Diagram of the components used for the dynamic dilution experiments. Two mass flow controllers (MFC) generated mixtures of H$_2$ in zero air (ZA), which passed through a Pt catalyst and needle valve or critical orifice before mixing with additional zero air. The resulting H$_2$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.
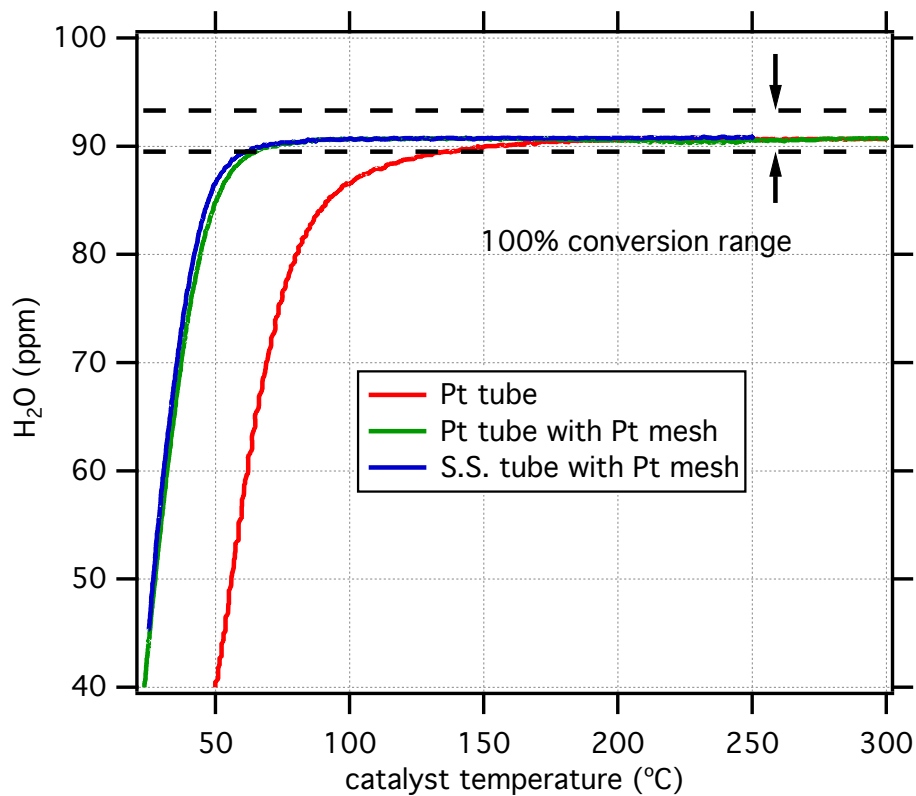
Fig. 2. Temperature dependence of conversion of H_2 to H_2O for 3 catalyst designs. Water vapor was measured with an MBW 373LX hygrometer.
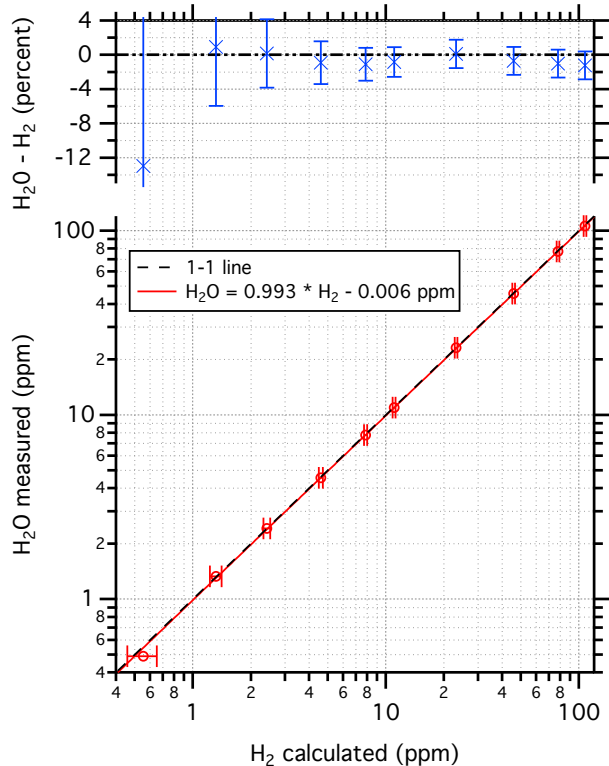
Fig. 3. Observed water vapor mixing ratios produced from a dynamic dilution of an H_2 / zero air mixture. Error bars represent the 2σ uncertainty in expected H_2O due to accuracy of the H_2 bottle (±0.75 %), 3 flow controllers (1 % each) and H_2O in zero air used for dilution (0.1 ± 0.1 ppm). Top panel: vertical range is selected to clearly show the uncertainty range for most of the points. The lowest concentration point (0.55 ppm) has an uncertaint of ±20 % which exceeds the range shown. Water vapor was measured with an MBW 373LX hygrometer.