

# REFERENCING DILUTION-BASED TRACE HUMIDITY GENERATORS TO PRIMARY HUMIDITY STANDARDS

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## ABSTRACT

We describe a technique for measuring the trace humidity level delivered by a permeation-tube type moisture generator (PTMG). Mole fractions of  $\text{H}_2\text{O}$  in  $\text{N}_2$  carrier gas in the range 10 nmol/mol to 100 nmol/mol were considered. The measurements are referenced to the NIST low frost-point generator (LFPG). A quartz crystal microbalance (QCM) hygrometer is used as a comparator to measure the concentration difference between the respective outputs of the PTMG and LFPG. Differences in the water vapor mole fraction of .1 nmol/mol were observable with this technique. Systematic differences with respect to the LFPG output of  $(3.8 \pm 0.9) \%$  and  $(2.9 \pm 0.7) \%$ , were measured for two PTMG devices.

## 1. INTRODUCTION

Water vapor present at trace levels in high-purity process gases (typically .100 nmol of  $\text{H}_2\text{O}$  per mol of gas mixture) is a ubiquitous contaminant that can adversely affect the fabrication of components for semiconductor, microelectronic, and photonic devices [1]. This fact has motivated the development and application of numerous techniques for the quantitation of trace humidity levels. Despite these many options, the real-time measurement and control of trace amounts of  $\text{H}_2\text{O}$  is challenging, and the prediction of an analyzer's response is usually fraught with uncertainty. In particular, sensor drift, non-linearity, hysteresis and other system-dependent effects demand that hygrometers be calibrated in the field against a transfer standard humidity generator.

Permeation tube moisture generators (PTMG) are commonly used by the semiconductor industry as portable transfer standards for the calibration of hygrometer systems. These devices are usually calibrated against primary or secondary gravimetric and flow rate measurement standards. Nevertheless, the traceability of various PTMG outputs to a common reference condition is not always straightforward. This can preclude quantitative comparisons among various realizations of the PTMG technique and provides an important motivation for the present work. To address these issues, here we demonstrate a particular approach by which the performance of PTMG transfer standards can be linked to a common reference standard humidity generator.

In this work, we measured the performance of PTMG transfer standards and used the NIST Low Frost-Point Humidity Generator (LFPG) as the reference standard humidity generator. Data were obtained for streams containing 10 nmol/mol to 100 nmol/mol of  $\text{H}_2\text{O}$  in  $\text{N}_2$  carrier gas. Below, we discuss the measurement principles, experimental configuration and measurement procedure, and we present and interpret experimental results characterizing two commercial PTMG devices.

## 2. GOVERNING EQUATIONS

The LFPG is the primary method at NIST for the generation of trace  $\text{H}_2\text{O}$  in inert gases and, given its thermodynamic basis and long-term stability, is an appropriate standard to which PTMG and other humidity generation devices can be linked. The mole fraction of water vapor generated by the LFPG is

determined by the saturator temperature,  $T_s$  and saturator pressure  $P_s$ , and is given by

$$x_L = f(T_s, P_s) e_w(T_s) / P_s \quad (1)$$

where  $f(T_s, P_s)$  is the enhancement factor of the gas mixture. The quantity  $e_w(T_s)$  is the saturation pressure of pure water vapor over a plane surface of hexagonal ice. The LFPG yields gas mixtures with H<sub>2</sub>O mole fractions that span the range 5 nmol/mol to 4 mmol/mol, with a repeatability of better than 0.2 %. Detailed descriptions of the apparatus are discussed elsewhere [2], and an assessment of the LFPG uncertainty is given in a separate paper appearing in this volume [3].

The PTMG uses flow dilution to produce a constant humidity level in a flowing gas stream. Under conditions of constant temperature, water vapor diffuses at a constant rate from the surface of a permeable tube containing liquid water, and this water vapor mixes with a metered stream of dry carrier gas. Assuming steady state and complete mixing of the two gas streams, the expected mole fraction of water vapor in the gas stream at the output of the PTMG is given by

$$x_p = \dot{n}_w / (\dot{n}_w + \dot{n}_c) + x_{bg} \approx \dot{n}_w / \dot{n}_c + x_{bg} = \dot{n}_w / (\dot{n}_c / M_c) + x_{bg} \quad (2)$$

where  $\dot{n}_w$  is the molar permeation rate of H<sub>2</sub>O. This quantity is usually determined by gravimetric methods. The term  $\dot{n}_c$  represents the molar flow rate of the carrier gas and is given by the ratio  $\dot{n}_c / M_c$ , where  $\dot{m}_c$  and  $M_c$  are the mass flow rate and the molecular mass, respectively of the carrier gas. The PTMG devices considered here are designed to operate at fixed temperature and variable mass flow rate of the carrier gas. In this manner, the mass flow rate is varied to adjust the mole fraction  $x_p$ . For completeness, Eq. (2) also includes the term  $x_{bg}$ , which represents any residual water vapor that might be present in the "dry" carrier gas. As discussed below, this background contribution can be important, especially at humidity levels approaching 1 nmol/mol.

### 3. UNCERTAINTY ANALYSIS

Assuming that the relative standard uncertainty in the flow rate measurement scales with  $\dot{n}_c^{-1}$ , an uncertainty analysis of Eq. 2 gives

$$u_f(x_p) = x_p^2 \beta_0 / x_0 = x_p^2 \beta_0 \dot{n}_c / M_c \dot{n}_w \quad (3)$$

for the standard uncertainty associated with the PTMG flow measurement. Here,  $x_0 = M_c \dot{n}_c / \dot{n}_w$ , and  $\beta_0$  corresponds to the relative standard uncertainty in the measurement of  $\dot{n}_c$  evaluated at the full-scale mass flow rate condition,  $\dot{n}_c = \dot{n}_0$ . The combined standard uncertainty  $u_c(x_p)$  in the PTMG mole fraction is obtained by the quadrature addition of  $u_f(x_p)$  with the standard uncertainty  $u_p(x_p)$ , where  $u_p(x_p)$  represents all other contributions to the uncertainty in the magnitude of  $x$  delivered by the PTMG. This latter uncertainty is assumed to be independent of  $x_p$ .

It is useful to define the quantity,  $\varepsilon = (x_p - x_L) / x_L$ , representing the fractional deviation between the mole fraction produced by the PTMG (given by  $x_p$ ) and the mole fraction produced by the LFPG (given by  $x_L$ ). In the limit of vanishing measurement error,  $\varepsilon$  will approach the relative error in the permeation

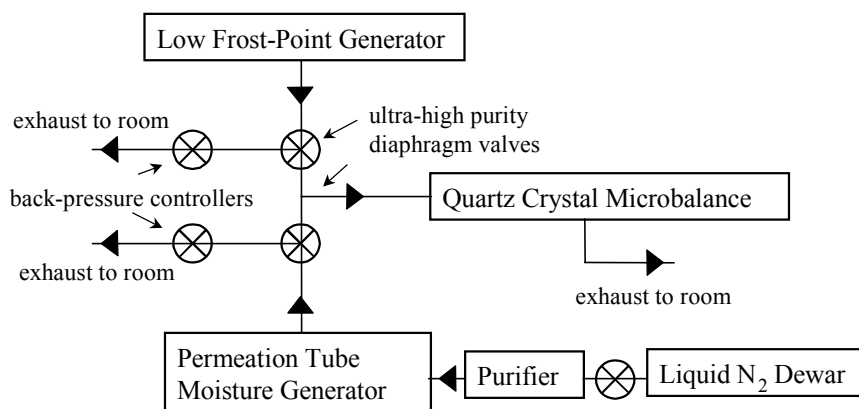
rate  $\dot{V}$ . Neglecting errors associated with the LFPG, the relative combined standard uncertainty in  $\varepsilon$  is

$$u_{r,c}(\varepsilon) = u_c(x_p) / x_p = \left[ x_p^{-2} (\beta_0 / x_0)^2 + u_p^2 / x_p^2 \right]^{1/2}. \quad (4)$$

Inspection of Eq. 4 indicates that  $u_{r,c}(\varepsilon)$  grows rapidly as  $x_0$ , and a broad minimum in  $u_{r,c}(\varepsilon)$  occurs at  $(x_0 u_p / \beta_0)^{1/2}$ . For large values of  $x_p$ ,  $u_{r,c}(\varepsilon)$  is proportional to  $x_p$ . This latter limit is a consequence of the increased measurement uncertainty in flow rate as the carrier gas flow rate is decreased. These effects are demonstrated below.

#### 4. DESCRIPTION OF EXPERIMENT

The comparator used for these measurements was a commercially available quartz crystal microbalance (QCM), which is based on a quartz crystal oscillator that is coated with a thin polymeric film. The response (*i.e.*, signal per unit mole fraction of H<sub>2</sub>O) of the QCM was nominally 70 mV (nmol/mol)<sup>-1</sup>.



**Figure 1:** Experimental configuration

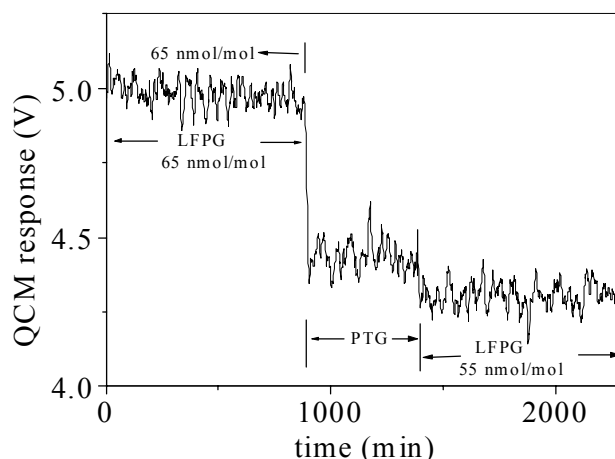
The system configuration, including the QCM comparator, the LFPG and PTMG under test, is shown schematically in Figure 1. The flow paths were designed so that nearly all of the tubing was continuously swept with gas from either the LFPG or the PTMG, and diaphragm valves were used to alternately isolate or connect the humidity generators to the hygrometer. Excess gas from the two generators was vented to the room through sufficiently long tubing to prevent back diffusion of water vapor to the hygrometer.

In order to optimize dry-down of the system, all-metal seals were employed, the dead space and surface area of all components were minimized, all tubing and components were made of internally electro-polished stainless steel, and bends in the tubing were completely avoided through the use of right-angle welded fittings.

Two back-pressure controllers maintained the manifold sample line pressure at an absolute pressure of  $-210$  kPa. This constant backpressure fixed the volumetric flow rate to the comparator at  $-200$  mL  $\text{Amin}^{-1}$  regardless of the flow coming from the LFPG or PTMG and minimized pressure-dependent H<sub>2</sub>O adsorption and desorption in the sample line. Although it was not insulated, the sample line was maintained at a constant laboratory temperature of  $-21^\circ\text{C}$ . The N<sub>2</sub> used for the PTMG carrier gas was supplied by a dewar containing liquefied N<sub>2</sub>. Prior to entering the PTMG, the N<sub>2</sub> gas was filtered by an in-line purifier to remove impurities, including trace water vapor before reaching the system. The manufacturer's

specifications for the in-line purifier indicate that the mole fraction of water vapor in the gas supplied to the PTMG was  $< 1$  nmol/mol. This amount is taken as an upper bound for  $x_{bg}$ .

Several  $\text{H}_2\text{O}$  concentrations, spanning the range  $x_p \approx 10$  nmol/mol to 100 nmol/mol, were considered for each PTMG. At each concentration, QCM measurements of the relevant sample streams were made in a three-step process. In the first and third steps, the LFPG temperature was adjusted to deliver a mole fraction of water vapor that bracketed the expected value from the PTMG. The full width of the bracketing interval typically ranged from 5 nmol/mol to 20 nmol/mol. In the second step, the QCM was used to measure the output of the PTMG. Through linear interpolation, these three QCM measurements were used to determine a measured value  $x_m$  for the PTMG. Each set of three QCM measurements was acquired back to back in time. The output signal from the QCM was monitored continuously to allow for system equilibration, signal averaging and identification of baseline drift. As an example, Figure 2 shows the QCM data for a case in which the PTMG-generated mole fraction is bracketed by the LFPG at 65 nmol/mol and 55 nmol/mol, respectively. These results illustrate that given sufficient averaging time, differences in water vapor mole fraction of .1 nmol/mol could be resolved.



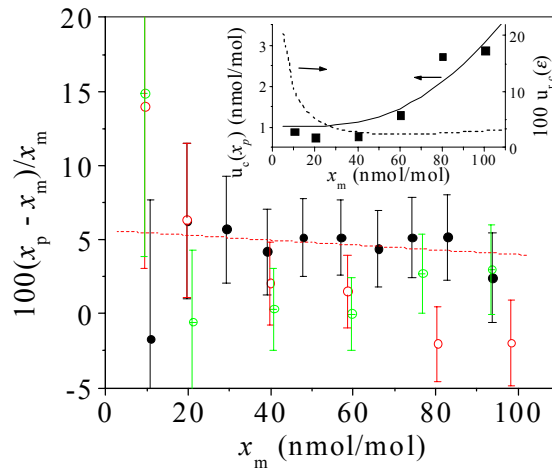
**Figure 2:** Time response of the QCM hygrometer successively exposed to streams from the LFPG, test generator and LFPG. The initial and final  $\text{H}_2\text{O}$  mole fractions were 65 nmol/mol and 55 nmol/mol, respectively, and induced QCM responses bracketing that of the unknown stream. Fluctuations in the QCM output (standard deviation of  $\sim 0.04$  V) had a period ranging from 20 min to 50 min.

Provided that the hygrometer has a linear response and exhibits little drift over the measurement time interval, the bracketing technique yields a result that is independent of the hygrometer responsivity. Thus, this approach eliminates any dependence upon the hygrometer's internal reference and the need for re-zeroing the sensor. For these reasons, we note that other hygrometers exhibiting good linearity, sufficiently rapid response and low short-term drift would be suitable for this application.

## 5. RESULTS AND DISCUSSION

Two permeation tube moisture generators having slightly different designs were tested. These devices, designated as PTMG *A* and PTMG *B*, were built by an instrument manufacturer and a semiconductor gas company, respectively. The permeation rates for tubes within devices *A* and *B* were previously calibrated by the owners and determined to be  $35 \text{ ng Amin}^{-1}$  and  $109 \text{ ng Amin}^{-1}$ , respectively. The mass flow meters of each PTMG were calibrated against NIST flow standards.

To assess the reproducibility of the technique, three sets of data were acquired for PTMG *A*, with each set spanning the range  $x_p = 10$  nmol/mol to 100 nmol/mol. For each operating condition, we determined the expected value of the PTMG-produced mole fraction using Eq. 2, and obtained a measured value of this quantity using the procedure outline above. Assuming  $x_m \approx x_L$ , then the quantity  $\varepsilon(x)$  was approximated by  $\varepsilon \approx (x_p - x_m)/x_m$ . The data sets were taken over an eight-month time interval, with each set taking approximately one week for completion. The first set of data (solid circles) was obtained by a different operator than the later two sets (open symbols). Although both operators used the same bracketing scheme as described in Fig. 2, different averaging times and bracketing widths were employed. The measurement results for PTMG *A* are summarized in Fig. 3. A background mole fraction of  $x_{bg} = 0.5$  nmol/mol was assumed for all cases. Each symbol set corresponds to a series of measurements spanning the concentration range. The dashed line is a linear regression to all of the data and has a slope  $= (-0.016 \pm 0.019)$  (nmol/mol)<sup>-1</sup>. The error bars are given by  $u_{r,c}(\varepsilon)$  and were estimated in the following way. As shown in the inset of Fig. 3,  $u_{r,c}(x_p)$  was found by grouping the measurements around the nominal values of  $x$  and computing a standard deviation from the ensembles. These data, shown in the inset of Fig. 3, were fit to Eq. 4. From this curve fitting procedure, we derive  $\beta_0 = 2.5 \times 10^{13}$ , in close agreement with the manufacturer's specified value of  $2.0 \times 10^{13}$ . Also, the curve fit yields the quantity  $u_p(x_p) \approx 1$  nmol/mol. This agrees closely with the measurement uncertainty discussed in Fig. 2.

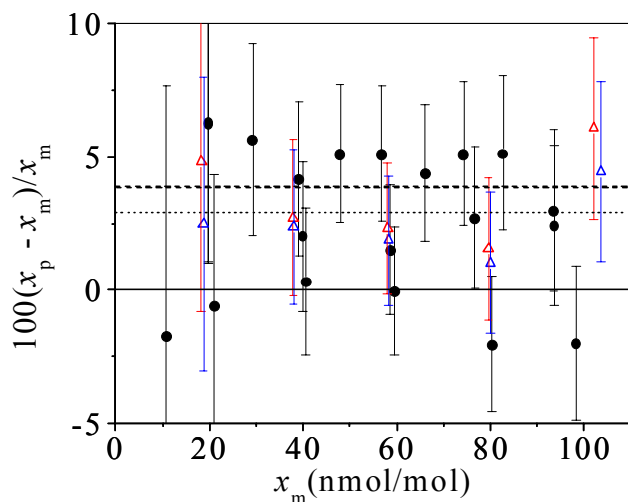


**Figure 3:** Measurement repeatability for PTMG *A*. The dashed line in the inset gives the error bars in the main figure. Also in the inset, the left axis shows the standard deviation of measured mole fractions, the square symbols correspond to the observed variations and the solid line is a least-squares fit to this data using Eq. 4, assuming  $x_p \approx x_m$ . Note the minimum in  $u_{r,c}(\varepsilon)$  occurs at  $x_p = 59$  nmol/mol.

A weighted linear regression to all of the data shown in Fig. 3, yields a nearly horizontal line with a slope given by  $-0.016$  (nmol/mol)<sup>-1</sup>. The 1-sigma uncertainty of the slope is greater than the slope magnitude, indicating that the trend in  $\varepsilon(x_m)$  is probably independent of  $x_m$ . Such behavior reveals a systematic error that can be attributed to the deviation between the measured and assumed values of  $x_p$ .

A summary of results for PTMG *A* and PTMG *B* is given in Fig. 4. Calculating the weighted averages, we find that  $\varepsilon = (3.8 \pm 0.9)$  %, and  $\varepsilon = (2.9 \pm 0.7)$  % for cases *A* and *B*, respectively. For PTMG *B*, the data pair corresponding to the  $x_m = 8$  nmol/mol condition (not shown) were treated as outliers, having

values of  $\varepsilon = 21.8\%$  and  $25.9\%$ , with  $u_{r,c}(\varepsilon) = 13\%$ . We speculate that small changes in  $x_{bg}$  would be influential at this condition.



**Figure 4:** Comparison of results for PTMG A (circles) and PTMG B (triangles). The dashed curves represent the respective average values of  $\varepsilon$ .

## 6. CONCLUSIONS

In this paper we have demonstrated a precise method for quantifying the performance of permeation tube moisture generators by direct comparison against a thermodynamic reference standard. We identified uncertainties in flow metering and background water vapor in the carrier gas as limiting effects. The method is capable of resolving fractional differences of the order of 1 %, for PTMG devices spanning the mole fraction range 10 nmol/mol to 100 nmol/mol.

## ACKNOWLEDGMENTS

The authors would like to thank W. Miller for his technical assistance and Ametek Corporation for the use of their quartz crystal microbalance. This work was partially supported by the NIST Office of Microelectronics Programs.

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