

Reducing the Uncertainty of Industrial Trace Humidity Generators through NIST Permeation-Tube Calibration

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Abstract Permeation-tube moisture generators (PTGs) are commonly used by the semiconductor industry as transfer standards for the calibration of hygrometer systems measuring trace amounts of water vapor in gases (water vapor mole fractions typically below 1×10^{-6}). They are relatively simple devices that generate a steady stream of humidified gas by diluting water vapor delivered at a constant rate from a permeable capsule with precisely metered purified gas, usually nitrogen. Here a new calibration service enabling the measurement of PTG permeation rates directly in terms of NIST primary standards of trace humidity generation is described. Rather than using commonly employed gravimetric methods for permeation-tube calibration, the method applied here links the permeation rate of the permeation tube to the thermodynamic properties of ice. Using a hygrometer based on cavity ringdown spectroscopy, we compare the water vapor concentrations produced by the NIST low frost-point generator (LFPG) and a specially constructed PTG containing the permeation tube undergoing calibration. A least squares fit of the data determines the permeation rate of the tube under test. We describe the calibration system, experimental procedure and present sample calibration data. The expanded relative uncertainty of NIST permeation-tube calibrations is 1.8% with a coverage factor $k = 2$, dominated by the Type A uncertainties.

Keywords Cavity ringdown · Frost point · Generator · Humidity · Permeation tube

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1 Introduction

Permeation-tube moisture generators (PTGs) are commonly used by the semiconductor industry as portable transfer standards for the calibration of hygrometer systems, and as internal calibration gas sources within humidity analyzers and mass spectrometers used for detecting multiple chemical species in gas distribution systems. They are relatively simple devices that generate a steady stream of humidified gas by diluting water vapor supplied at a constant rate from a permeable capsule with precisely metered purified gas, usually nitrogen. With the exception of a few specialized components, PTGs are constructed from commonly available high-purity valves, fittings, electro-polished tubing, and flow controllers. As a result, PTGs are easily constructed and relatively inexpensive to produce.

Permeation tubes, the source of water vapor in the PTG, require calibration since the permeation rate cannot be confidently predicted from material properties and geometry alone. For specific tubes, the permeation rate is usually determined by maintaining the tube in a dry, temperature-controlled environment, and by repeated weighing over a time interval that is long enough to measure the change in tube mass. However, such measurements can become quite time consuming, exhibit high uncertainty, and limit the accuracy of PTGs encountered in high-purity applications.

The calibration technique presented here constitutes an alternative to gravimetric permeation rate measurements. It provides traceability to NIST primary humidity standards and links the permeation rate of specific permeation tubes to the thermodynamic properties of ice.

2 PTG Governing Principles

The PTG technique 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 conditions and complete mixing of the two gas streams, the expected mole fraction of water vapor in the gas stream at the output of the PTG in the dilute limit is

$$x_p(T_p, \dot{n}_c) = \frac{\dot{n}_w(T_p)}{\dot{n}_c} + x_{p,b} \quad (1)$$

where $\dot{n}_w(T_p)$ is the molar permeation rate of water at the permeation-tube temperature T_p and \dot{n}_c represents the molar flow rate of the carrier gas. For completeness, Eq. 1 also includes the term $x_{p,b}$, which represents any residual water vapor that might be present in the “dry” carrier gas plus any systematic deviation from the above model employed to predict the water-vapor concentration generated by the PTG. As discussed below, this background contribution can be important, especially at humidity levels approaching $1 \text{ nmol} \cdot \text{mol}^{-1}$ (equivalent to 1 part-per-billion). The PTG devices considered here are designed to operate at a fixed temperature and variable flow rate of the carrier gas. In this manner, the flow rate \dot{n}_c is varied to adjust the mole fraction x_p .

3 Combined PTG Uncertainty

From Eq. 1, the uncertainty in x_p , given by $u(x_p)$, can be expressed in terms of the uncertainty in the permeation rate $u(\dot{n}_w)$, uncertainty in the flow rate of the carrier gas $u(\dot{n}_c)$, and uncertainty of the background water vapor $u(x_{p,b})$. The effect of uncertainty in $x_{p,b}$ on the combined uncertainty is greatest for relatively low values of x_p . At the highest water concentrations generated by a particular PTG system, the uncertainty in \dot{n}_c is usually the most problematic, because the carrier-gas flow rates are a small fraction of their full-scale values and, hence, the relative uncertainty, $u_r(\dot{n}_c)$, is high. While uncertainties in $x_{p,b}$ and \dot{n}_c affect the accuracy of PTGs at the operational limits, the relative uncertainty in permeation rate by gravimetric determination is typically of the order of 10% and affects the entire PTG operating range, motivating more accurate methods for establishing \dot{n}_w .

4 Apparatus

The NIST permeation-tube calibration system (PTCS) evolved from the experimental method developed for the NIST-SEMI Intercomparison of PTGs [1,2], and is designed to provide a stable, efficient apparatus suitable for the routine calibration of permeation tubes. Briefly, the technique uses a stable humidity analyzer as a nulling device, alternately sampling the respective outputs of two humidity generators and allowing one generator's output to be expressed in terms of a standard generator's output and the difference in analyzer response. The subsystems of the PTCS, shown schematically in Fig. 1, are discussed below. They include the low frost-point generator (LFPG), a custom-built PTG, a gas manifold connecting the humidity generators in parallel to a single trace-humidity analyzer, and the analyzer.

The LFPG is the primary method at NIST for the generation of low levels of water in inert gases and, given its thermodynamic basis and long-term stability, is an appropriate reference humidity standard. 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

$$x_L = f(T_s, P_s)e_w(T_s)/P_s \quad (2)$$

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 water mole fractions that span the range from $5 \text{ nmol} \cdot \text{mol}^{-1}$ to $4 \text{ mmol} \cdot \text{mol}^{-1}$. References [2] and [3] provide detailed descriptions of the LFPG.

Compared to industrial PTGs, the PTG subsystem of the PTCS incorporates improvements in temperature control and flow measurement which render it particularly suitable for high-precision comparisons with the LFPG. This PTG subsystem is shown schematically in Fig. 1. Permeation tubes under calibration are placed inside a cylindrical, electro-polished stainless-steel cavity 1.65 cm in diameter and 21 cm in length. The cavity and an upstream heat exchanger are embedded inside two aluminum plates and bonded to the plates with epoxy potting compound. Figure 2 shows a sectioned

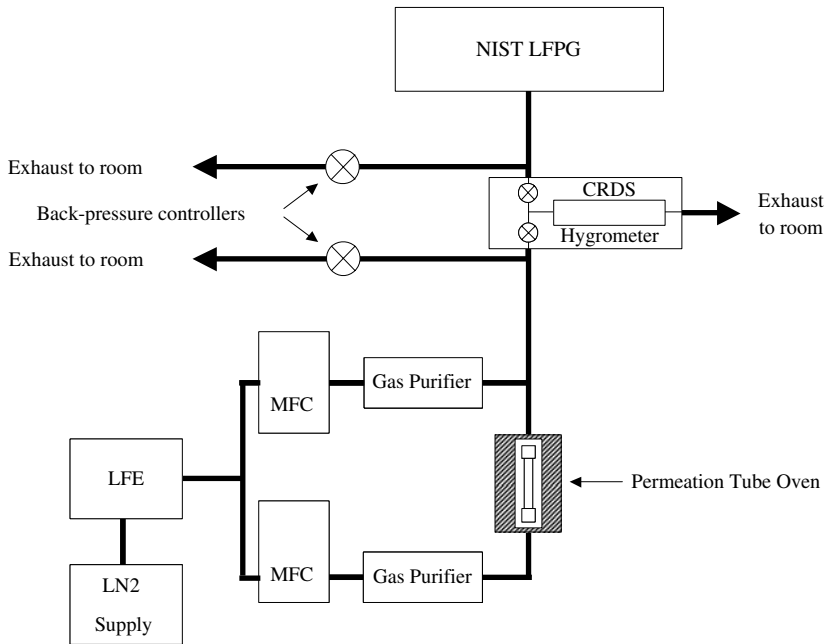


Fig. 1 Schematic diagram of the NIST PTCS

view of the cavity, heat exchanger, and aluminum oven. The oven resides within a foam enclosure and is kept at constant temperature by resistance heaters bonded to the top and bottom faces of the oven. During use, a constant stream of purified N_2 flows through the heat exchanger, where it is warmed to the oven temperature. The gas stream, at a flow rate of nominally $200 \text{ standard cm}^3 \cdot \text{min}^{-1}$ (sccm, at a temperature of 0°C and pressure of $101,325 \text{ Pa}$), flushes the oven of the water vapor emitted by the permeation tube, sending it downstream for mixing with a second carrier gas stream.

Dilution gas supplied by a liquid N_2 -containing Dewar enters the PTG flow system through two stages of pressure regulation. The gas is filtered and then passed through a commercially available laminar-flow element (LFE). The LFE used for a particular operating condition measures the combined flow rate of the constant oven-flushing gas and the variable diluent gas stream. Thus, only one flow-metering device contributes to the flow-measurement uncertainty. After measuring the total flow rate, the flow is split and the respective flow rates are controlled by two high-purity mass flow controllers (MFCs). Once diverted and metered (but prior to entering the oven in the case of the oven stream), both gas streams are purified using commercial semiconductor-grade gas purifiers. Purification of the gas streams after metering effectively eliminates contributions to $x_{p,b}$ from the LFEs and MFCs. As mentioned earlier, the purified nitrogen stream that flows over the permeation tube remains constant in order to maintain constant heat loading on the oven, while the second nitrogen stream is varied in order

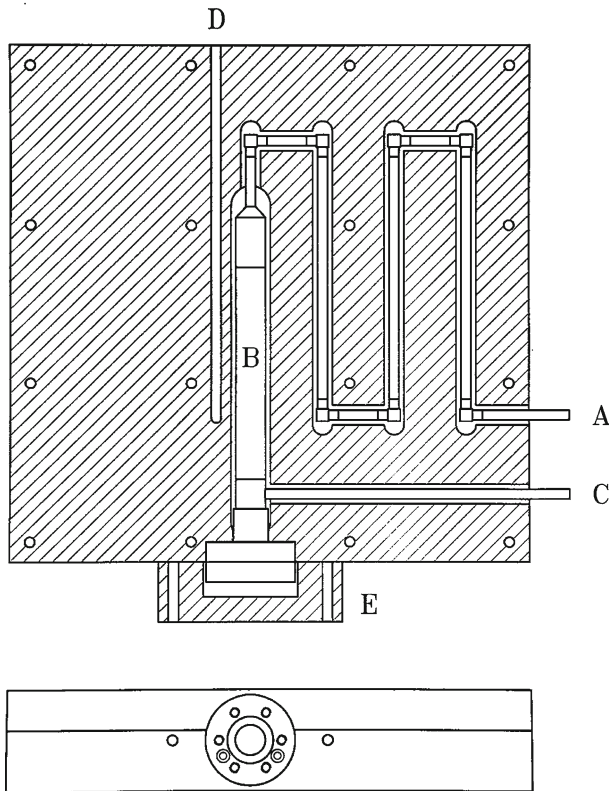


Fig. 2 Sectioned view of the PTG oven: A—oven heat exchanger; B—permeation-tube cavity; C—oven exit; D—thermometer well. Access to the cavity is depicted in the end view. During operation, an aluminum cap E covers the cavity access, and the oven is surrounded by insulation

to produce desired water-vapor concentrations. The two gas streams are recombined immediately downstream of the oven and sent to the analyzer or vented to the room.

A pair of electro-polished, stainless-steel manifolds connects the humidity generators in the PTCS to a high-sensitivity analyzer. The gas pressure in both the LFPG and PTG manifolds is kept constant and at nominally the same value by a pair of electronic back-pressure controllers, ensuring that the gas load on the analyzer is the same from either humidity generator. Within the analyzer, a computer-controlled sampling system selects between the two gas streams. When not being measured by the analyzer, the gas flowing from the “idling” generator exhausts into the room.

A hygrometer employing cavity ringdown spectroscopy (CRDS) as the sensing technology was chosen as the analyzer in the PTCS. The CRDS hygrometer responds rapidly to changes in water-vapor concentration and exhibits good stability and linearity. Sensitivity, speed of response, and stability are the most important hygrometer attributes for the measurement technique; we determine the hygrometer sensitivity during the permeation-tube calibration.

5 Permeation-Tube Calibration Technique

Preparation steps for calibration of permeation tubes include installation of the permeation tube within the PTG oven, LFPG and analyzer preparation, and subsystem dry-down. Since placing the permeation tube in the oven exposes the oven interior to the laboratory environment, the oven must be subsequently purged with purified N_2 and allowed to reach thermal equilibrium at the desired temperature prior to calibration. The manifold downstream of the PTG and the analyzer itself are also purged with purified N_2 . Since the LFPG runs continuously, no additional preparation is required other than adjusting the gas pressure within the LFPG and its connection manifold to match that of the PTG, and adjusting the LFPG to produce an appropriate water-vapor concentration. The CRDS hygrometer is configured to sequentially sample each humidity generator, and the analog output is scaled to cover the expected range of humidity in the calibration. Prior to the calibration, the frequency of the laser within the CRDS hygrometer is tuned according to the manufacturer's recommendations.

The outputs from both generators are sequentially compared at several humidity points spanning the range of the PTG/permeation tube combination. The analyzer first measures the water concentration delivered by the PTG, while the nitrogen stream from the LFPG is exhausted into the laboratory. The temperature of the LFPG saturator is then adjusted to produce a water-vapor concentration that is nominally in the center of the expected humidity range that can be produced by the permeation tube/PTG combination. After the analyzer reaches equilibrium with the test gas from the PTG, the gas streams are switched so that the analyzer samples the LFPG output. This set of two independent observations constitutes a data pair which, when repeated over a range of water concentrations, gives a set of data pairs that can be used to quantify the unknown permeation rate, as given below. During early tests of the PTCS, the output of both humidity generators was closely matched, in order to minimize the effects of short-term changes in analyzer sensitivity. Experience has shown that the analyzer response is sufficiently linear to support a simpler experimental technique, in which the LFPG is adjusted to only one or two water-vapor concentrations during the course of the calibration.

6 Experimental Results and Calculation of Permeation Rate

We completed a series of nine independent calibrations of a single permeation tube at $T_p = 50^\circ\text{C}$ over 15 months to demonstrate the performance of the PTCS. Within each calibration, three to twelve independent data pairs were realized, spanning the water mole fraction range from 20 to 80 $\text{nmol} \cdot \text{mol}^{-1}$ in nearly uniform steps of 20 $\text{nmol} \cdot \text{mol}^{-1}$. We obtained data pairs sequentially, in order of increasing or decreasing wetness.

The permeation rate of the tube considered above was determined from the data pairs using the following approach. Let S_L and S_P represent the measured response of the analyzer to the LFPG and PTG outputs, respectively. Assuming that the analyzer responds linearly with respect to the water mole fraction of each sample stream, then S_L and S_P are given by

$$S_L = a(x_L(T_s, P_s) + x_{L,b}) + S_0, \quad (3)$$

and

$$S_p = a(x_p(T_p, \dot{n}_c) + x_{p,b}) + S_0, \quad (4)$$

where a and S_0 are the analyzer sensitivity and zero offset, respectively. For each data pair, we determine the value for a experimentally during measurements of the LFPG output, and assume that it remains constant for the time required to perform the pair of measurements. The quantities $x_{L,b}$ and $x_{p,b}$ correspond to residual water background acquired in the manifold connecting the respective humidity generators and analyzer, plus any background produced within the analyzer itself, and any systematic deviation from the model employed to predict the water-vapor concentration generated by either humidity generator. Both background terms are assumed to be constant over the time interval required to obtain the data pair. Defining $y_p = \dot{n}_c^{-1}$ as the reciprocal molar flow rate of the carrier gas and $\delta x_b = x_{L,b} - x_{p,b}$ as the difference in water background levels, subtraction of Eq. 4 from Eq. 3 gives the measured quantity,

$$S_L - S_p = \Delta S = a(x_L(T_s, P_s) - \dot{n}_w(T_p)y_p + \delta x_b) \quad (5)$$

Equation 5 may be rewritten as

$$x_L(T_s, P_s) - \frac{\Delta S}{a} = \dot{n}_w(T_p)y_p - \delta x_b, \quad (6)$$

where the unknown values of the molar water permeation rate, \dot{n}_w , and background difference, δx_b , are expressed in terms of the water-vapor concentration produced by the LFPG, the measured difference in the humidity produced by the two humidity generators, and the flow rate of N_2 through the PTG. We obtain values for \dot{n}_w and δx_b using a linear least squares fit of Eq. 6 to the data. Table 1 contains the results of the nine calibrations, reported in nanograms per minute, a customary unit within the semiconductor process gas industry for the water emission rate from permeation tubes.

The experimental method evolved throughout the course of the tests. The first measurements, performed in September of 2005, were obtained using a quartz crystal micro-balance (QCM) as the humidity analyzer. In these measurements, we closely matched the water-vapor concentration produced by the two humidity generators, reducing the sensitivity of the calibration to analyzer nonlinearity and instability. A CRDS hygrometer replaced the QCM in July of 2006. Measurements from July followed the same procedure as those of September 2005, although the analysis performed with substantially reduced sensitivity and increased noise ($5 \text{ nmol} \cdot \text{mol}^{-1}$, peak to peak) compared to the QCM; retuning of the laser immediately before the November 2006 tests greatly improved performance. The difficulty in determining humidity generator and analyzer equilibrium in the July 2006 data explains the difference between these results compared to the nearly identical results obtained in September 2005 and November 2006. We employed two different methodologies during the tests of

Table 1 Emission rates obtained between September 2005 and November 2006

	Run no.	Emission rate from linear fit ($\text{ng} \cdot \text{min}^{-1}$)	Percent uncertainty in fit ($k = 1$)	Degrees of freedom
Sep-05	1	48.7	0.5	3
	2	48.6	0.3	3
	3	48.5	2.7	1
Jul-06	1	48.9	1.4	2
	2	50.5	0.8	4
	3	49.1	0.9	5
Nov-06	1	48.9	0.8	3
	2	48.3	0.6	10
	3	47.7	0.5	10

November 2006. During runs 1 and 2, the output of the PTG was varied as before, while the output of the LFPG was fixed at $60 \text{ nmol} \cdot \text{mol}^{-1}$. During Run 3, we matched the LFPG output to the output of the PTG as per the original experimental procedure. The similarity of the calibration results in this series of three calibrations supports the use of the simplified procedure of Runs 1 and 2.

For each calibration run, Table 1 also includes the standard uncertainty of the fit and the number of degrees of freedom. The fit uncertainty scales approximately with the number of degree of freedom, as

$$u(\text{fit}) = \frac{C}{\sqrt{\text{df}}}, \quad (7)$$

where df is the number of degrees of freedom and $C = 1.57$, as obtained from a weighted average of the fit uncertainties in Table 1.

The residuals obtained by comparing the measurement data from November 2006 with the calculated values of \dot{n}_w and δx_b are plotted in Fig. 3, and show no significant correlation with flow rate. Independent measurements of the water-vapor backgrounds, x_{bg} , produced by the two systems of combined humidity generator and connecting manifold show that the magnitude of the background is less than $0.4 \text{ nmol} \cdot \text{mol}^{-1}$, but variable depending on factors including laboratory temperature, convective currents within the laboratory, and analyzer behavior. In fact, the value for x_{bg} may be zero during periods of water adsorption onto the internal surfaces of the system of generator, tubing, and analyzer. The magnitude of the fit residuals is approximately the same as independently measured values of x_{bg} , suggesting that the variability of the background difference, δx_b , during the calibration is a major contributor to uncertainty in the fit.

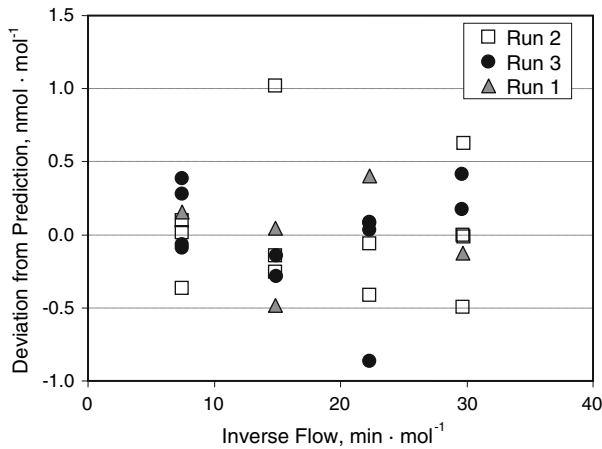


Fig. 3 Difference between the measured value of $x_L(T_s, P_s) - \frac{\Delta S}{a}$ and $\dot{n}_w(T_p) y_p - \delta x_b$ calculated using values for \dot{n}_w and δx_b obtained from a linear least squares fit of Eq. 6. The magnitude of the residuals shows no significant correlation with flow rate through the PTG

Table 2 Relative uncertainty components for calibration of the permeation rate \dot{n}_w , expressed as a percent of \dot{n}_w

Uncertainty type	Relative uncertainty component	Magnitude (%)
B	Permeation-tube temperature	0.1
B	PTG flow measurement	0.2
B	LFPG and correlated sensitivity coefficient	0.8
A	Linear fit with degrees of freedom = 4	1.6
Combined expanded relative uncertainty ($k = 2$)		1.8

7 Calibration Uncertainty

The combined expanded uncertainty of the PTCS is 1.8%, dominated by Type A uncertainty in \dot{n}_w . The uncertainty components and their magnitude are listed in Table 2 and discussed below.

7.1 Type B Uncertainties

The fractional combined, expanded uncertainty (coverage factor $k = 2$) of the LFPG over the humidity range considered here is 0.8%, and is documented in [4]. Since the analyzer sensitivity, a , is determined by comparing the hygrometer response to the calculated humidity based on measured temperature and pressure within the LFPG saturator, $\frac{\Delta S}{a}$ is highly correlated with the LFPG. From Eq. 6 it can be shown that the fractional uncertainty in permeation rate contributed by $U_r(x_L(T_s, P_s) - \frac{\Delta S}{a})$ is 0.8% ($k = 2$).

The flow rate of diluent N_2 through the PTG is measured by a laminar-flow element. While the PTCS contains two flow elements, they cover different flow ranges and only one is used at a time. The manufacturer's stated combined expanded uncertainty for the laminar-flow elements used in the PTCS is 0.2% ($k = 2$), contributing 0.2% to the relative uncertainty in permeation rate.

A high-precision temperature controller supplies heat uniformly to the top and bottom surfaces of the oven in response to a feedback signal provided by a 100 Ω platinum resistance thermometer mounted in the aluminum block. Following calibration of the controller and thermometer, an expanded uncertainty of 0.023°C is achieved for the uncertainty of the permeation tube temperature. The emission rate of water from a permeation tube is an exponential function of temperature. For an oven temperature of 80°C, the fractional uncertainty in permeation rate due to the temperature uncertainty is 0.13% ($k = 2$).

7.2 Type A Uncertainties

The least squares fit provides estimates of the statistical uncertainties of the \dot{n}_w and δx_b parameters. The value for δx_b is only of interest in that the calculated value should approximate previously obtained direct measurements of water-vapor backgrounds and is not considered directly in the uncertainty analysis. We use Eq. 7 to estimate the uncertainty in \dot{n}_w , as discussed above. Based on four degrees of freedom, corresponding to six independent data points per calibration, the standard relative uncertainty of \dot{n}_w is 0.8% ($k = 1$).

8 Conclusion

Permeation tubes may now be calibrated by the NIST primary trace humidity standard, thus providing the most direct traceability possible for industrial humidity generators. It is expected that the PTGs employing NIST-calibrated permeation tubes will have uncertainties up to 10 times smaller than current PTG uncertainties. The resultant industry-wide availability of more accurate humidity reference data will improve trace humidity measurement, enabling analyzer manufacturers to develop new, better trace measurement technologies and increase confidence and uniformity in these measurements throughout the semiconductor industry.

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