

Errors in Rate-of-Rise Gas Flow Measurements from Flow Work

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Abstract

The rate-of-rise (RoR) method determines flow by measuring the time rate of change of the amount of gas in a collection tank of known volume as it is filled via a flow meter under test. The mass of gas is calculated from time-stamped pressure and temperature data and accurate RoR measurements require reliable gas pressure and temperature values while the collection tank is filling with gas. We present a thermodynamic model and experimental measurements of gas temperature errors that are a function of a dimensionless ratio related to: {the heat transfer from the gas to its surroundings} / {the heat generated by flow work}. The uncertainty of RoR flow measurements made using the NIST 34 L collection tank is <0.12 % for flows between 1 sccm* and 200 sccm. At lower and higher flows, the RoR uncertainty rises to approximately 1 % due to leaks and temperature errors induced by flow work.

1. Introduction

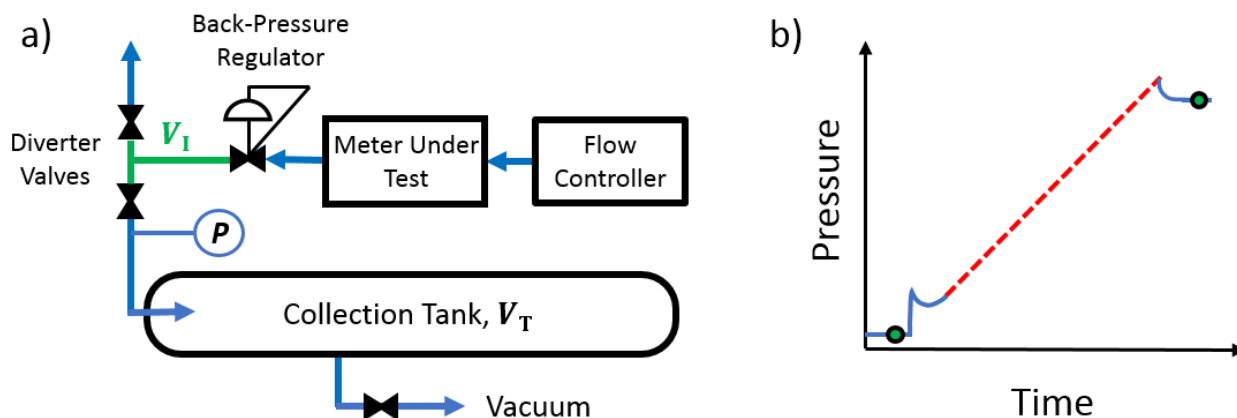


Figure 1. a) Components of NIST's *PVTt* and Rate-of-rise (RoR) flow standard. b) Time-dependent pressure measured during a calibration by both methods. For the RoR calibration, the mass flow $\dot{m}_{RoR}$ is calculated from the slope of the red dashed line; the initial and final transients (blue curves) are ignored. For a *PVTt* calibration, the initial and final masses are calculated from the pressure data before and after the transients (green circles). The mass difference is divided by the total filling time.

* sccm = standard cubic centimeters per minute (cm^3/min) with reference conditions of 101.325 kPa and 0°C and slm = standard liters per minute (L/min) at the same reference conditions.

The rate-of-rise (RoR) method calculates the rate of change of mass during the tank filling process via the equation:

$$\dot{m}_{\text{RoR}} = \frac{d}{dt} [(V_T + V_I) \rho(P, T)] = \frac{N \sum_{j=1}^N t_j m_j - \sum_{j=1}^N t_j \sum_{j=1}^N m_j}{N \sum_{j=1}^N t_j^2 - \left(\sum_{j=1}^N t_j \right)^2}, \quad (1)$$

where V_T is the collection tank volume, V_I is the inventory volume between a back-pressure regulator and the diverter valves, P and T are the pressure and temperature of the collected gas, and t is time. The real gas density $\rho(P, T)$ can be calculated from the NIST properties database REFPROP [1]. The latter part of Equation 1 is the slope of the mass-versus-time record, as determined using a first order least squares regression [2] with N mass values evenly spaced in time where $m_j = (V_T + V_I) \rho(P_j, T_j)$. The RoR method is a dynamic volumetric method because the pressure and temperature measurements are made while their values are changing, not at steady state. RoR can be applied to a collection tank that is used as a sink (as described above) or as a source. A similar apparatus can be used to make Pressure-Volume-Temperature-time ($PVTt$) flow measurements, as explained in Section 2.

To calibrate a flow meter, data from the meter under test are collected and averaged over the same time interval that the RoR or $PVTt$ measurements are made. Valves allow the collection tank to be evacuated by a vacuum pump and then filled with a flow through the meter under test (Figure 1). Note that for RoR measurements, the collection volume is $V_T + V_I$, where V_I is the inventory volume.

The RoR method has been used by the semiconductor manufacturing industry for many years to calibrate mass flow controllers using chemical vapor deposition chambers as the collection tank [3]. NIST has applied the RoR method at flows below 100 sccm using our 34 L $PVTt$ collection tank. When used for $PVTt$ measurements, the 34 L collection tank is normally filled from vacuum to 100 kPa, but if this were done for a flow of 1 sccm, the filling would take 24 days! The RoR method allows us to gather calibration data for small gas flows in a shorter time, so that a typical RoR calibration at one flow set point will gather 1 h of pressure and temperature data at 10 second intervals.

In this paper, we will document details of the RoR data collection and processing, explain the reasons for observed differences between RoR and $PVTt$ flow measurements made at NIST, and give an uncertainty analysis for the RoR method. Our goal is to provide guidance on how to design and use a RoR standard to obtain low uncertainty measurements of small gas flows.

2. NIST Implementation of $PVTt$ Standards

The 34 L $PVTt$ gas flow standards measure the time to fill the collection tank from 0.020 kPa to a “full” condition, usually 100 kPa. The operation and uncertainty of the $PVTt$ standards is documented in detail elsewhere [4, 5] and is only briefly summarized here. Diverter valves are used to switch flow from the meter under test into the collection tank. The temperature and pressure measurements of the gas in the collection tank under steady state conditions, before and after filling, are used to calculate the gas density (green circles in Figure 1). Flow is calculated using the equation:

$$\dot{m}_{PVTt} = \frac{V_T(\rho_T^{(f)} - \rho_T^{(i)}) + V_I(\rho_I^{(f)} - \rho_I^{(i)})}{t^{(f)} - t^{(i)}} , \quad (2)$$

where (i) and (f) indicate initial and final values respectively. The *PVTt* method must account for pressure and temperature changes in the inventory volume between the meter under test and the collection tank. At NIST this is done by using an inventory “mass cancellation” technique that ensures that the initial and final density in the inventory volume are equal, $\rho_I^{(f)} = \rho_I^{(i)}$ [5]. In contrast, the RoR method is applied during intervals where pressure and temperature in the collection tank are unaffected by the switching of the diverter valves (red dashed line in Figure 1). The RoR method has the advantage that it does not use the extra instrumentation, data acquisition, and processing required to implement mass cancellation. In addition, for a collection tank of a given size, RoR enables low flow measurements in a much shorter time than static flow measurement standards such as the *PVTt* method.

The volume of the 34 L collection tank was measured gravimetrically with an uncertainty of $< 0.012 \%$ *. The NIST *PVTt* flow standards and their uncertainty of 0.025% have been validated by numerous inter-laboratory comparisons. Here, the *PVTt* flow measurements will be used as the reference to evaluate the RoR method.

The 34 L collection tank is submerged in a temperature controlled water bath with a set point equal to the nominal room temperature, $T_{H_2O} = 296.463$ K. A proportional-integral-derivative feedback controller, recirculation pumps, and baffles provide temporal and spatial uniformity of the water bath temperature of ± 0.002 K. It is difficult to accurately measure the temperature of the gas in the collection tank because of the low heat capacity of the gas relative to temperature sensors and the poor heat transfer between them. It is easier to make a low uncertainty temperature measurement of the recirculating, high-heat-capacity water bath. For *PVTt* flow measurements, we wait 10 minutes after filling to achieve thermal equilibrium between the gas and the surrounding water and measure T_{H_2O} to obtain the temperature of the gas in the collection tank with an uncertainty of 0.012 K. We note that the collection tank has a diameter of only 15 cm to improve heat transfer and reduce the time necessary to obtain equilibrium.

The time constant for thermal equilibrium of the gas in the full collection tank is < 170 s. It was determined by filling the collection tank and recording the time necessary for the pressure to equilibrate (Figure 2). Flow work (heat of compression) elevates the temperature of the gas in the collection tank during filling [6]. After the filling stops, the pressure declines as the gas returns to thermal equilibrium with the water bath. Mass conservation dictates that the average gas density remains constant during the thermal equilibration process. The decreasing pressure correlates with the decreasing gas temperature, and the time required for pressure stabilization determines the thermal time constant.

Figure 2 illustrates equilibration following a flow of 5 slm. In this case, the temperature of the gas is approximately 2.5 K warmer than the water bath after filling. The gas temperature while the

* All uncertainties herein are $k = 2$, approximately 95 % confidence level.

collection tank is filling is an important uncertainty component for RoR flow measurements. A thermodynamic model for the temperature difference between the gas and water T_{err} (see Section 5) reveals that T_{err} is related to a dimensionless ratio that determines the heat transfer from the gas to its surroundings relative to the heat generated by flow work.

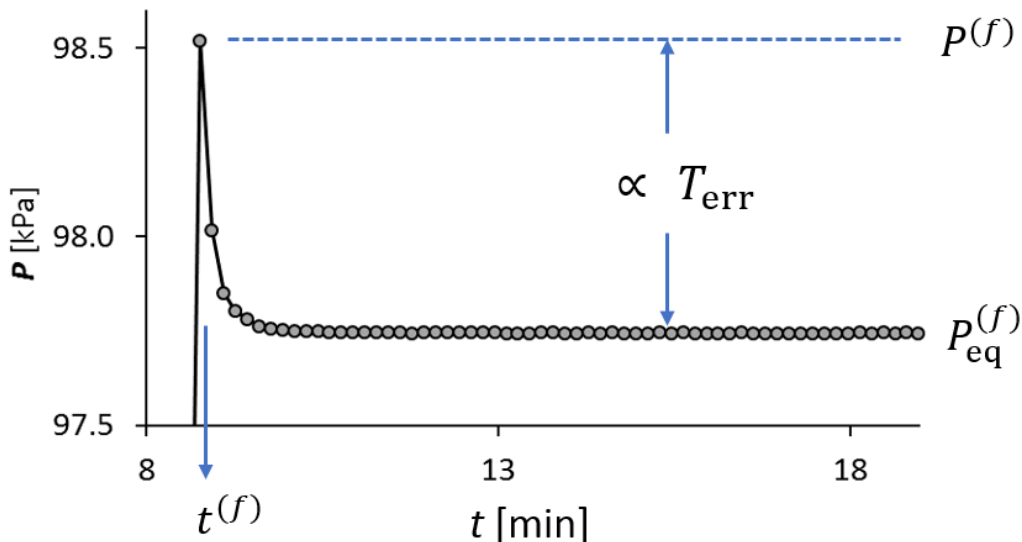


Figure 2. Pressure in the 34 L collection tank as a function of time for an air flow of 5 slm. The gas is initially warm (and therefore at higher pressure) due to flow work during filling. After filling stops at the time $t^{(f)}$, the gas temperature comes to equilibrium with the water bath with a time constant of 170 s.

3. Comparison of RoR and $PVTt$ Flow Measurements

Figure 3 shows the difference between $PVTt$ and RoR methods when applied to the same data sets. The RoR method is applied over a shorter time interval than the $PVTt$ method: transient pressure data caused by opening the diverter valve are excluded from the RoR processing. The effects of the different time intervals have been removed by using data from the meter under test as an intermediary to normalize the data from the two techniques. The RoR flows in Figure 3 assume that the gas is in thermal equilibrium with the water bath and there is no pressure drop between the pressure sensor and the tank (discussed in Section 4). The RoR results agree with $PVTt$ flows near zero, but the difference increases linearly to 0.3 % near 1000 sccm. Because of data like these, the NIST RoR system has only been used to report flows < 100 sccm. In this paper, we develop a RoR uncertainty analysis that explains the differences in Figure 3 and shows how to avoid them. For the purposes of this research, we used the 34 L tank to make RoR measurements up to 10 slm, one hundred times the normal maximum.

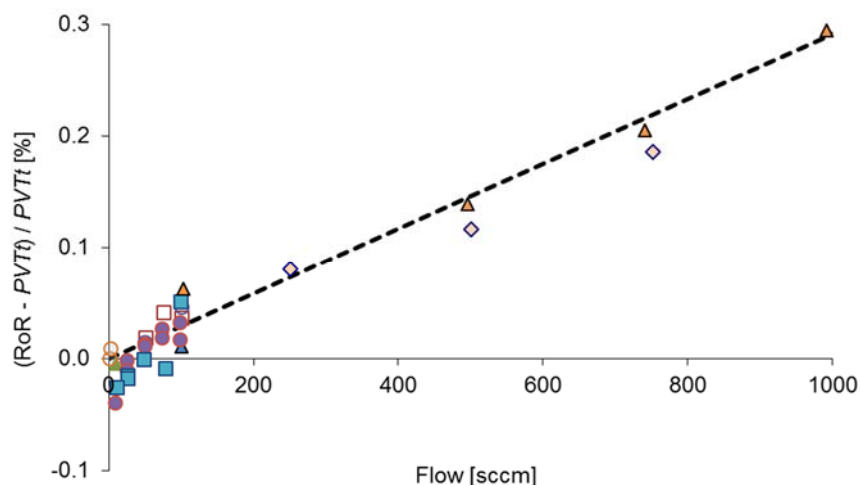


Figure 3. Fractional differences between Rate-of-rise and $PVTt$ flow measurements made with the 34 L collection tank. The dashed line shows the fractional differences between the two methods predicted by temperature errors caused by flow work, T_{err} (dashed line in Figure 6).

Assuming ideal gas behavior, a stable zero offset in the pressure measurement introduces no error in RoR flow measurements. Density is proportional to pressure and, because the slope calculated in Equation 1 depends on pressure differences, a zero offset in pressure cancels. However, density varies inversely with temperature, and therefore a zero offset in temperature does not cancel. A temperature offset T_{err} causes a fractional RoR mass flow error of T_{err}/T . Our experiments show that the difference between the RoR and $PVTt$ flows shown in Figure 3 is predominantly caused by errors in the temperature measurement of the gas while the tank is filling. The flow work and resulting temperature errors increase with increasing flow. In Section 5 we will study the temperature errors in more detail.

4. Pressure Errors, P_{err}

Although zero offsets in pressure do not lead to RoR flow uncertainty, any pressure error that does not remain constant while the tank is filling will introduce RoR flow error. Two examples of non-constant pressure errors are: (1) gain (span) errors of the sensor calibration, and (2) non-linearity in the pressure measurements. Here non-linearity means that the measured pressure is not proportional to the actual pressure in the tank. The pressure sensors used in the NIST 34 L flow standard have excellent linearity under steady state pressure conditions; however, their pressure readings during filling depend on the flow and the pressure in the tank. The piping between the pressure sensor and the tank causes a pressure drop (P_{err}) that decreases as the tank fills.* The changing pressure drop introduces a non-linearity to the pressure measurements that cause a RoR flow error. Another possible cause of significant pressure non-linearity, addressed in Section 5, is an increase in the sensor's temperature due to flow work.

* The head correction because the pressure sensor is not located at the same elevation as the tank is another such source of non-linearity, but it is $< 0.01\%$ for the 34 L system.

To accurately estimate the pressure drop, we constructed a full-scale model of the inlet piping (Figure 4a). The model reproduced the lengths of pipe and elbows between the tap for the pressure sensors and the collection tank. We measured the pressure drop with a differential pressure sensor for flows between 1 slm and 10 slm and for “tank” pressures between 11 kPa and 100 kPa (Figure 4b and c). Both flow and tank pressure influence the pressure drop. The pressure errors (and resulting RoR flow errors) are larger for larger flows and for smaller tank pressures. Using the data in Figure 4b, a RoR flow measurement at 10 slm that filled the tank from 11 kPa to 100 kPa will have a non-linearity introduced by the changing pressure drops of $137 \text{ Pa} - 16 \text{ Pa} = 121 \text{ Pa}$. This pressure non-linearity will lead to a flow measurement error of $0.121 \text{ kPa} / 89 \text{ kPa} = 0.14 \%$. If data for pressures between 30 kPa and 100 kPa are used instead, the RoR flow error is reduced to $0.035 \text{ kPa} / 100 \text{ kPa} = 0.05 \%$. If the pressure drop as a function of flow and tank pressure were well characterized, it would be practical to correct the pressure measurements. Also, a better position of the pressure tap (i.e. on the tank itself instead of the inlet piping) would probably avoid significant errors due to pressure drop. We have not yet done so because the plumbing change would necessitate a new volume determination for the 34 L tank.

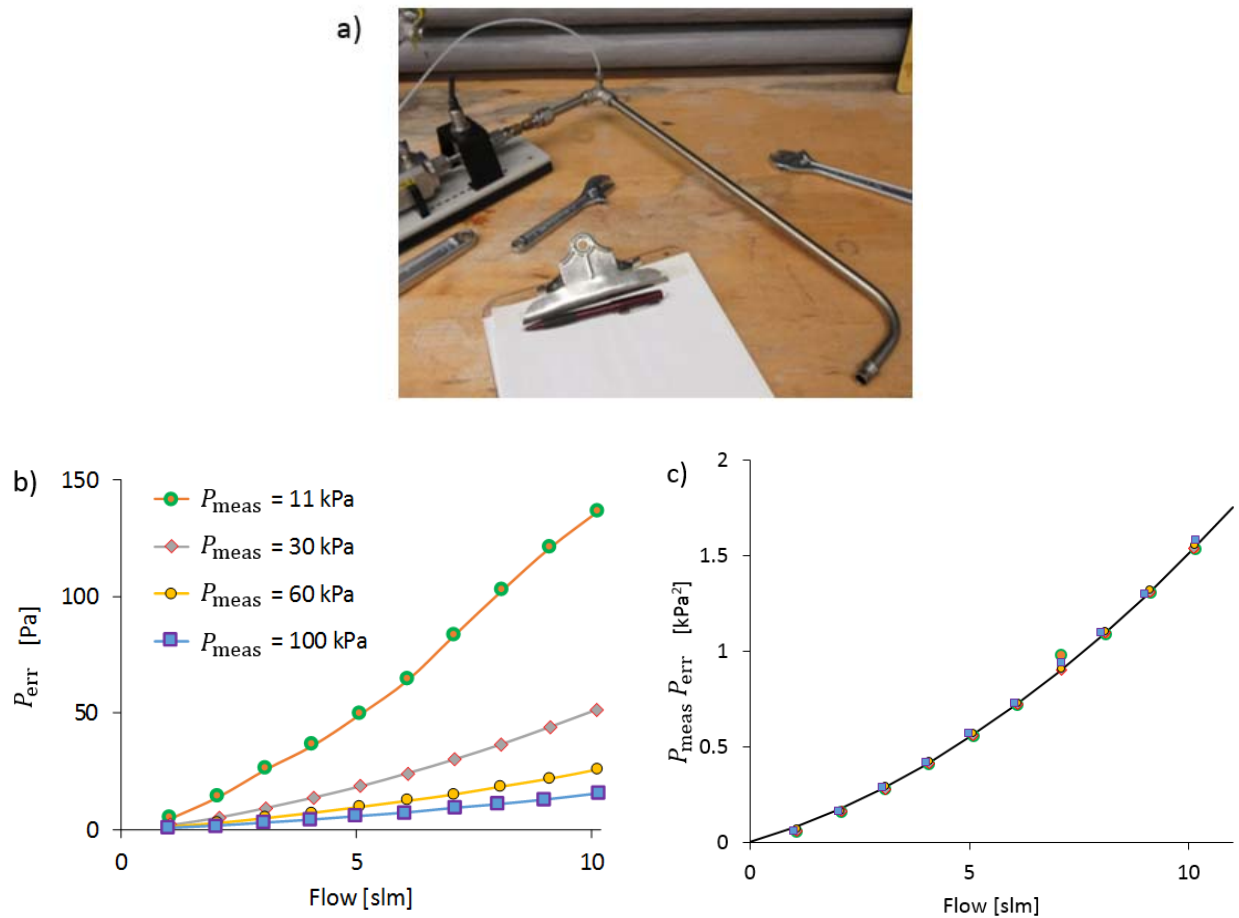


Figure 4. a) The reproduction of the 34 L tank inlet piping, b) the pressure drop *versus* flow for various tank pressures, and c) the product of the measured tank pressure and pressure drop *versus* flow.

The function,

$$P_{\text{err}} = b_1 \frac{\dot{m}}{P_{\text{meas}}} + b_2 \frac{\dot{m}^2}{P_{\text{meas}}} \quad , \quad (3)$$

was used to fit the experimental data in Figure 4 with residual standard deviation of 2.2 Pa. In Equation 3, $\dot{m}$ is the mass flow, P_{meas} is the measured tank pressure, and b_1 and b_2 are best-fit coefficients. The functional form of Equation 3 is expected for laminar flow in a tube with other loss sources (in this case elbows). The P_{err} measurements are based on a reproduction of the tank inlet plumbing, not the actual piping, so they are not used to make corrections to the RoR pressure measurements. Here, the P_{err} fit is used to experimentally determine temperature measurement errors and during the RoR uncertainty analysis.

5. Temperature Errors from Flow Work, T_{err}

Flow work heats the gas in the collection tank during filling and causes the gas temperature to exceed that of the water bath. The availability of *PVTt* flow measurements from the NIST 34 L system allows experimental assessment of these temperature errors. The experimental data validate our thermodynamic model of flow work for the RoR standard and guide future RoR system design and application.

The measurements of temperature errors use the collection tank as a “gas thermometer”: assuming a constant mass flow entering the tank, we can use the RoR and *PVTt* data to calculate the pressure that would be present in the tank P_{eq} if the gas were in equilibrium with the surrounding water bath. Then the ratio of the measured tank pressure to P_{eq} can be used to calculate the actual average temperature of the gas during filling:

$$T = \frac{P_{\text{T}}}{P_{\text{eq}}} T_{\text{H}_2\text{O}} = \frac{(P_{\text{meas}} - P_{\text{err}})}{P_{\text{eq}}} T_{\text{H}_2\text{O}} \quad , \quad (4)$$

where $T_{\text{H}_2\text{O}}$ is the temperature of the water bath, P_{meas} is the pressure measured by the calibrated pressure transducers connected to the collection tank, P_{err} is the pressure drop calculated from Equation 3, and $P_{\text{T}} = P_{\text{meas}} - P_{\text{err}}$ is our best estimate of the pressure in the filling tank. (The gas is assumed to be ideal throughout this analysis.)

The estimate of P_{eq} is determined so that the RoR flow matches the *PVTt* flow calculation. For a steady flow of an ideal gas, $P_{\text{eq}}(t)$ varies linearly with time and is expressed by

$$P_{\text{eq}}(t) = P_{\text{eq}}^{(i)} + \frac{dP}{dt} (t - t^{(i)}) = P_{\text{eq}}^{(i)} + \left[\frac{P_{\text{eq}}^{(f)} - P_{\text{eq}}^{(i)}}{t^{(f)} - t^{(i)}} \right] (t - t^{(i)}) \quad , \quad (5)$$

where the superscripts (i) and (f) indicate the initial (start) and final (stop) conditions of the collection. The equilibrium pressure of the full tank $P_{\text{eq}}^{(f)}$ is available by waiting for the gas to return to thermal equilibrium with the surrounding water (see Figure 2 or 4).

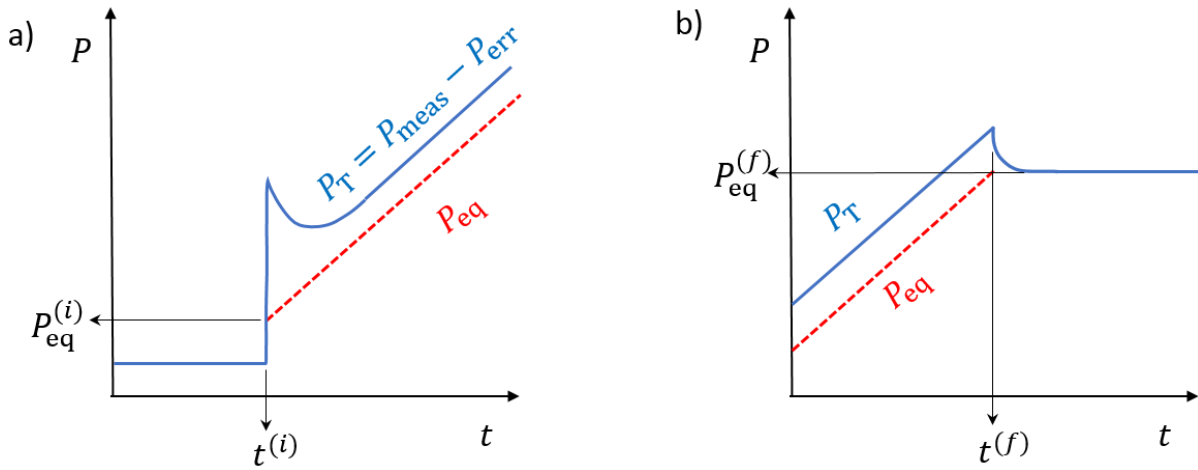


Figure 5. Plots of pressure versus time for the a) start and b) stop of the collection tank filling labelled with quantities used to experimentally determine temperature errors T_{err} caused by flow work in the RoR system.

The initial equilibrium pressure $P_{eq}^{(i)}$ is not equal to the pressure in the collection tank before filling because there is a sudden in-rush of gas from the inventory volume. Hence $P_{eq}^{(i)}$ includes mass from three sources:

$$P_{eq}^{(i)} = \frac{[m_T^{(i)} + m_I^{(i)} + m_{DE}^{(i)}] R_u T_{H_2O}}{M(V_T + V_I)} , \quad (6)$$

where R_u is the universal gas constant, and M is the gas molar mass. The initial mass of gas in the collection tank $m_T^{(i)}$ and in the inventory volume $m_I^{(i)}$ are calculated from pressure and temperature values gathered for the $PVTt$ flow measurements, before the gas is diverted to the tank, under conditions of thermal equilibrium:

$$m_T^{(i)} = \frac{P_T^{(i)} V_T M}{R_u T_{H_2O}} \text{ and } m_I^{(i)} = \frac{P_I^{(i)} V_I M}{R_u T_{H_2O}} . \quad (7)$$

The third mass component $m_{DE}^{(i)}$ is the mass of gas that accumulates in the inventory volume during the “dead-end” time Δt_{DE} [4] when both $PVTt$ diverter valves are closed at the start of a collection (< 100 ms). It also is calculated from values available from the $PVTt$ system:

$$m_{DE}^{(i)} = \dot{m}_{PVTt} \Delta t_{DE} . \quad (8)$$

We used the approach described above to calculate temperature errors $T_{err} = T - T_{H_2O}$ for experiments conducted in the 34 L system at flows of 100 sccm, 500 sccm, 1 slm, 5 slm, and 10 slm and the results are plotted in Figure 6. Note that we intentionally applied the RoR method to larger flows than normal to better examine the temperature errors. Also, data were recorded at 10 Hz during these experiments (instead of the normally used 0.1 Hz) for better time resolution at the higher flows. For the 5 slm and 10 slm flows, critical flow venturis (CFVs) were used as the

meter under test. For flows of 5 slm or less, Molbloc[®] laminar flow meters were used as the meter under test. In general, meters under test are sensitive to pressure and to fluctuations of the flow. Therefore, RoR measurements are conducted with a back pressure regulator installed between the laminar flow meter and the collection tank. The back-pressure regulator maintains a steady pressure in the test section while the tank pressure increases during a fill. When the back-pressure regulator is installed (for flows ≤ 1 slm), the maximum collection pressure is 50 kPa rather than 100 kPa.

In Figure 6, there are two sets of data for 10 slm, one using a critical flow venturi (CFV) with throat diameter of 0.39 mm and an inlet pressure of 770 kPa and another using a 0.65 mm CFV and 295 kPa. There is no significant difference between the T_{err} traces for the two different CFVs.

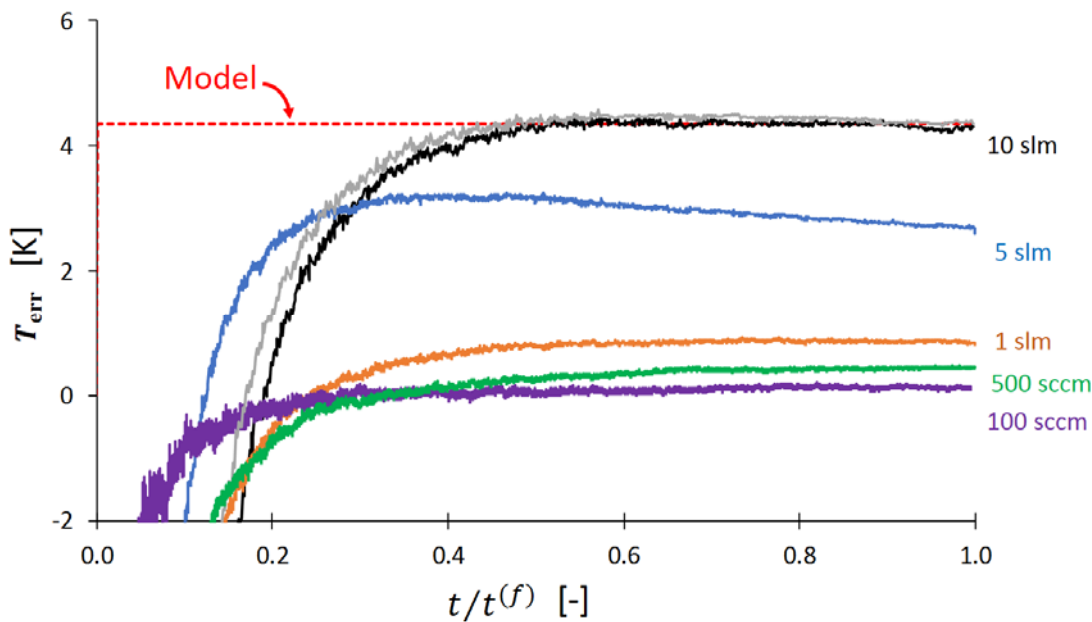


Figure 6. Temperature errors in the 34 L system during a RoR measurement for flows from 100 sccm to 10 slm. The data for 10 slm were taken with two critical flow venturis, one with a throat diameter of 0.39 mm and the other with a diameter of 0.65 mm.

Our lumped parameter thermodynamic model applies conservation of mass and energy to the filling tank [see Section 9 and reference 6]. It predicts that the temperature error is:

$$T_{err} = T - T_{H_2O} = T_{H_2O} \left[\frac{(T_{in}/T_{H_2O})^{\gamma-1}}{1 + \Gamma} \right] \left[1 - \left(\frac{\dot{m}t}{m^{(i)}} + 1 \right)^{-(1+\Gamma)} \right], \quad (9)$$

where T is the gas temperature in the tank, T_{in} is the temperature of the gas entering the tank from the meter under test, γ is the ratio of the specific heats at constant pressure and constant

* Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

volume ($= c_p/c_v$), $\dot{m}$ is the mass flow, $m^{(i)}$ is the initial mass of gas in the tank before filling begins, and t is the time since the filling began. The dimensionless quantity Γ is defined by:

$$\Gamma \frac{(T - T_{\text{H}_2\text{O}})}{T} = \left[\frac{hA}{c_v \dot{m}} \right] \left[\frac{(T - T_{\text{H}_2\text{O}})}{T} \right], \quad (10)$$

where A is the surface area of the collection tank and h is the convective heat transfer coefficient between the gas and the tank walls. Equation 10 is the ratio of {heat transfer from the gas to its surroundings} to {the energy input to the gas by flow work}. The lumped-parameter analysis (Section 9) assumes that the gas is well stirred and that the tank wall temperature matches the water bath temperature, so that the heat transfer from the gas to the tank walls is the limiting heat transfer process.

Both the thermodynamic model and the pressure-equilibration data show that the temperature difference between the gas and the water bath reaches a steady state value during later portions of the fill and T_{err} is larger for larger flows (due to increased flow work). Unfortunately, values for the heat transfer coefficient are not readily available, but the model predictions for T_{err} using a value of h that forces agreement with the 10 slm steady state T_{err} are plotted in Figure 6. The model predicts that the temperature difference rapidly reaches a steady state value (< 0.2 s), but the experimental values in Figure 6 (based on pressure measurements made with a Heise HPO* sensor) show time constants of up to 8 min to reach steady state T_{err} values. We note that the lumped model does not account for the time required for convection to develop in the collection tank nor the transient response of the pressure sensor.

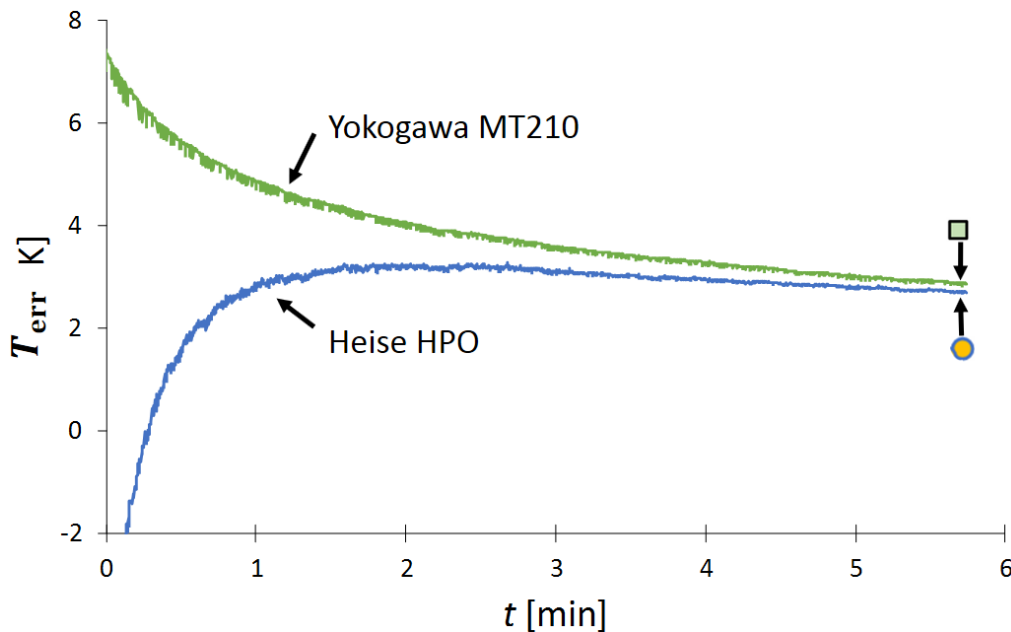


Figure 7. Temperature errors for 5 slm inferred from two sensors used to measure the tank pressure. The endpoints (indicated by symbols) are plotted for this and other flows in Figure 8.

Figure 7 implies that the transient response of the pressure sensor is important. The T_{err} traces based on two pressure sensors, the Heise HPO sensor used in Figure 6 and a Yokogawa MT210 pressure sensor, are quite different during earlier portions of the filling process. There are several phenomena that directly affect the time-dependence of the pressure sensor, such as 1) its mechanical and electrical response times, 2) the conductance of the tube connecting the sensor to the collection tank, and 3) flow-work-induced changes in the sensor's temperature. We hypothesize that the sensors in Figure 7 responded differently to these phenomena due to their different insulation or temperature control systems.

While Figure 7 shows that the pressure sensor's transient response can cause an error early in the fill process, it and analogous plots for other flows show that the T_{err} traces converge with the passage of time. Therefore RoR data from late in the fill process are less prone to errors caused by the response of pressure sensors to transients. Figure 8 plots T_{err} measured at the end of the collection *versus* flow: the plotted values correspond to the T_{err} values in Figure 6 where $t/t^{(f)} = 1$. Steady state values of T_{err} calculated from the Yokogawa MT210 pressure sensor agree well with those calculated from a Heise HPO pressure sensor.

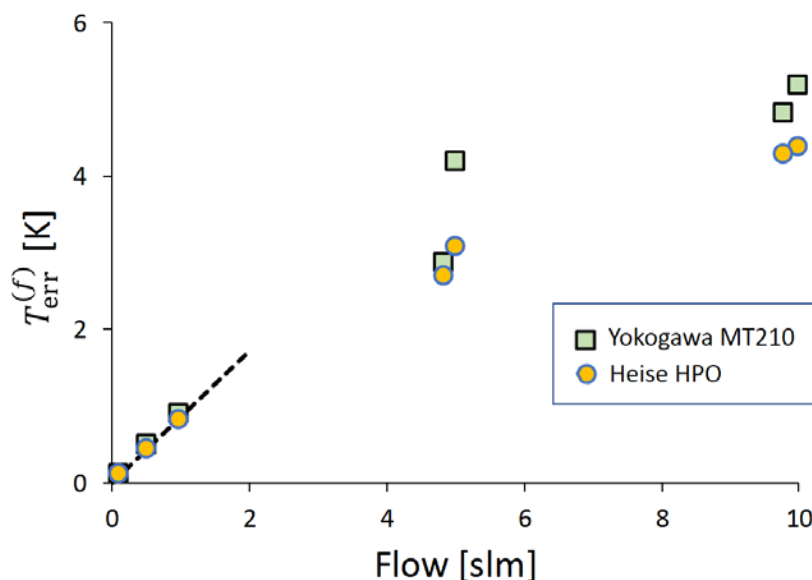


Figure 8. Difference between the gas temperature in the 34 L collection tank and the water bath temperature at the end of a RoR collection. The dashed line was used to produce the predicted RoR versus $PVTt$ difference in Figure 3.

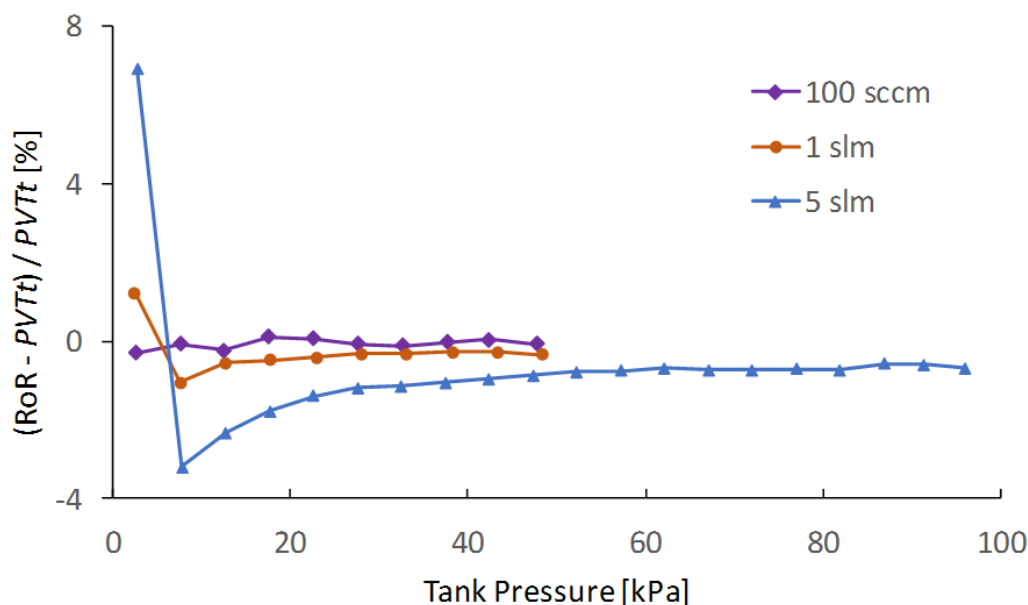


Figure 9. Difference between RoR and *PVTt* flow measurements using different portions of the data record, *i.e.* empty to 5 kPa, 5 kPa to 10 kPa, etc. The difference at high flows and low pressures is caused by pressure sensor response to transient conditions and pressure drop P_{err} .

Figure 9 compares RoR flow measurements for different portions of the filling process with the *PVTt* flow measurements. At lower tank pressures and larger flows, the errors in the RoR results are more than 5 %. As one would expect from Figure 6, as time passes and the tank reaches higher pressures, the RoR flow errors reach a steady value. Larger T_{err} and P_{err} values cause larger RoR flow uncertainties at larger flows (if uncorrected).

6. Uncertainty Analysis

The uncertainty of RoR gas flow measurements made using the NIST 34 L collection tank is plotted in Figure 10. The temperature and pressure errors T_{err} and P_{err} are treated as uncertainties (not corrections) in this analysis. For flows between 0.001 slm and 0.2 slm, the 34 L RoR flow standard has uncertainty between 0.05 % and 0.12 %.* For this range of flows, the dominant uncertainty varies between leaks, repeatability of the best existing device (BED), the collection volume, and density. At flows < 0.001 slm, the uncertainty is primarily due to the leak corrections and at flows > 0.2 slm, the RoR flow uncertainty is dominated by the uncorrected temperature errors T_{err} .

* All uncertainties herein are $k = 2$, approximately 95 % confidence level values.

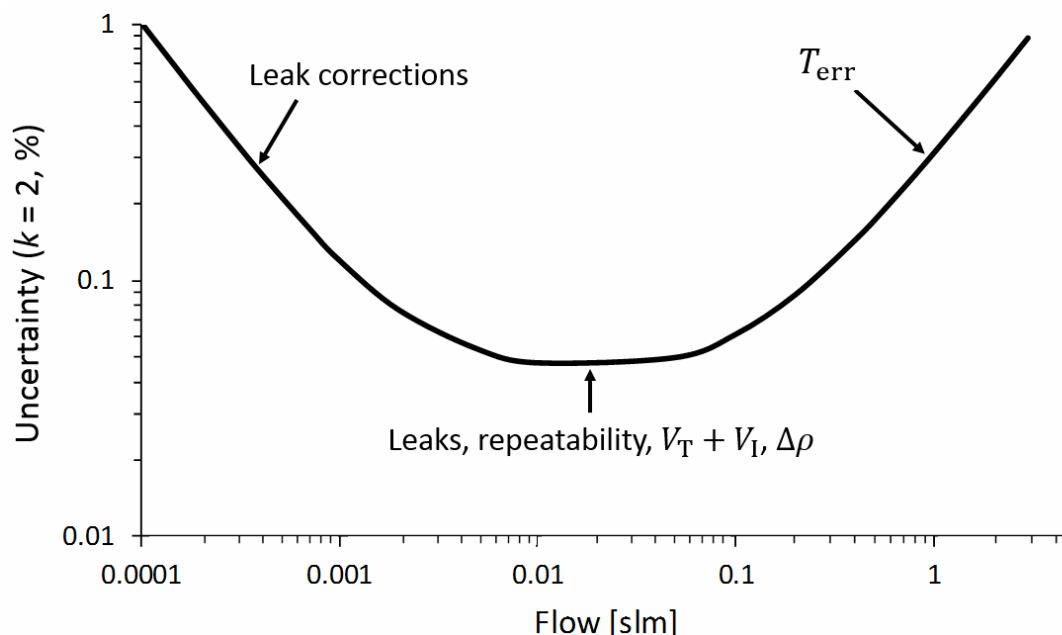


Figure 10. Uncertainty ($k = 2$, approximately 95 % confidence level) versus flow for the NIST 34 L Rate-of-rise flow standard.

The uncertainty components included in the analysis are:

1. Volume of the collection tank: $U(V_T + V_I)$ is 9.7 cm³ or 0.028 % [5].
2. Calibration, drift, and resolution of pressure, temperature, and time measurements: The pressure in the collection tank is measured with a pair of sensors that have an uncertainty of 0.006 kPa for pressures between 20 kPa and 130 kPa, are linear within 0.001 kPa over the same range, and have a resolution of 0.001 kPa. The RoR system is used at pressures greater than 20 kPa where the pressure sensors are known to be linear and transients in their readings due to the in-rush of gas (seen in Figures 6 and 7) have diminished to negligible levels, i.e. the time response of the pressure, temperature, and meter under test are not a concern due to proscribed operating conditions. The uncertainty of the water bath temperature is 0.012 K and the time uncertainty is 0.001 s.
3. Density calculations: The uncertainty of the compressibility factor (20 parts in 10⁶) and molar mass (40 parts in 10⁶) are included along with pressure and temperature uncertainties. The uncertainty of the universal gas constant is negligible (< 1 part in 10⁶).
4. Leaks: The leak for the 34 L system has been measured for a range of tank pressures. The RoR flow measurements are corrected using a fit to the leak versus pressure data. The uncertainty of the leak correction is 5×10^{-4} sccm.
5. Repeatability of the BED is based on the standard deviation of the mean for calibration results from laminar flow meters.
6. Slope calculation: The uncertainty in calculation of slope is insignificant if data are collected for a sufficiently long interval. The uncertainty in the mass values m_j in Equation 1 is at

least 2.5 times larger than the uncertainty in the time values t_j , allowing us to apply the simplest expression for the expanded uncertainty of the slope calculation [2]:

$$U(a_1) = 2 \left[\frac{\frac{\sum_{j=1}^N (m_j - a_1 t_j - a_0)^2}{N-2}}{\frac{\sum_{j=1}^N t_j^2 - \frac{(\sum_{j=1}^N t_j)^2}{N}}{N}} \right]^{\frac{1}{2}} = \frac{4\sqrt{3} s(m)}{\sqrt{N^3 - N} \Delta t}, \quad (11)$$

where a_0 and a_1 are the zeroeth and first order coefficients of the fit to the mass versus time data. (Here we have used a_1 instead of $\dot{m}_{\text{RoR}}$ to avoid confusion: Equation 11 gives the uncertainty related to the fitting process, not the total uncertainty of the RoR mass flow.) The quantity $s(m)$ is the sample standard deviation of the mass fit residuals and Δt is the time interval between successive mass measurements. We used example data sets to quantify $s(m)$ for a range of flows and it led to < 0.01 % uncertainty contribution to the RoR mass flow.

For the NIST 34 L tank, a minimum of 1 h of 0.1 Hz data ($N = 360$ points) are processed to produce one RoR flow measurement. At flows below 1 sccm, data are collected for 18 h or more ($N \geq 6480$) so that the pressure change is ≥ 1 kPa in order to avoid problems due to the uncorrelated uncertainty of the pressure and temperature sensors. This is necessary because the normalized sensitivity coefficients $(x_i/\dot{m})(\partial\dot{m}/\partial x_i)$ for the pressures and temperatures used in the RoR calculation are inversely proportional to $P_N - P_1$. To illustrate the issue, consider the simplified case of a RoR measurement based on only two points, $m_1 = (V_T + V_I) \rho(P_1, T)$ and $m_2 = (V_T + V_I) \rho(P_2, T)$ separated by $\Delta t = t_2 - t_1$ so that $\dot{m}_{\text{RoR}} = (m_2 - m_1)/\Delta t$. If the 95 % confidence level uncertainty due to non-linearity of the pressure sensor is 0.001 kPa, $P_1 = 20$ kPa, and $P_2 = 20.1$ kPa, this uncorrelated pressure uncertainty would lead to a mass flow uncertainty of $0.001 \text{ kPa} / (20.1 \text{ kPa} - 20 \text{ kPa}) = 1$ %. By filling the tank longer to increase the pressure change (and increase N), this uncertainty is reduced.

7. Uncertainty caused by flow instability is negligible. At NIST, we use a mass flow or pressure controller to ensure that the flow from the meter under test is stable within 0.2 % or better. Any data showing transients due to out-of-control environmental temperatures are removed prior to processing. Uncertainty due to flow instability is negligible because the meter under test has a short time response compared to the averaging interval (≥ 1 h) and because the RoR and meter under test data are averaged over the same interval. To visually qualify data that will be used to calculate the mass flow by Equation 1, we first plot the RoR flow calculated by:

$$\dot{m}_{\text{RoR},j} \cong (V_T + V_I) \left[\frac{\rho(P_{j+1}, T_{j+1}) - \rho(P_j, T_j)}{t_{j+1} - t_j} \right], \quad (12)$$

The results from Equation 12 must be filtered (e.g. by a moving average of 10 or 100 points) to reduce noise from pressure resolution (Figure 11).

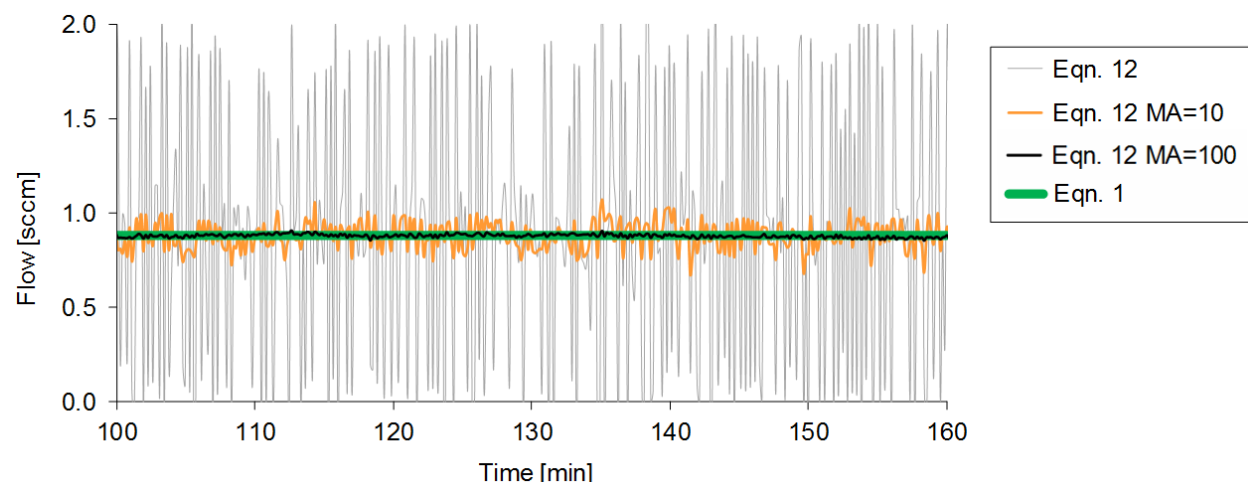


Figure 11. Example RoR flow from the best fit (Equation 1), and from Equation 12 with different moving average (MA) windows applied to check data for flow stability.

8. T_{err} , P_{err} : No corrections for the pressure drop between the pressure sensor and the collection tank P_{err} or for the temperature difference between the water bath and the gas T_{err} are made in the NIST RoR standard. At flows above 0.2 slm, the uncertainty increases because of P_{err} , T_{err} , and the decreasing number of data points N . The uncertainty at flows > 0.2 slm is predominantly due to T_{err} , not P_{err} , but the errors introduced by pressure drop can be significant for poorly selected operating conditions, i.e., if one filled the tank from empty to only 5 kPa at flows > 1 slm where the P_{err} and dP_{err}/dP are large (Figure 4).

Calculating the uncertainty due to the errors in temperature and pressure is complicated by the fact that T_{err} and P_{err} have asymmetric probability distributions and are correlated (both are tank pressure and flow dependent). They are asymmetric because we know that they always have positive values. In different circumstances, one might choose to treat T_{err} and P_{err} as corrections rather than errors or uncertainties. We have chosen not to use them as corrections in this case* because we do not intend to use RoR measurements for flows above 0.2 slm. (We will use $PVTt$ measurements instead.) We emphasize the importance of quantifying these error sources. Methods for handling asymmetric uncertainty distributions are available [2], but for simplicity, we calculated the error in density change that would result from T_{err} and P_{err} for the particular flow and tank pressure conditions of interest and added that error to the root-sum-of-squares of all other components.

7. Advice for Designers and Operators of RoR Standards

A well designed RoR system will minimize the temperature rise due to flow work. This can be done by using a tank that has the characteristics of a heat exchanger: made of a thermally conductive material with large surface area. A water bath surrounding the collection tank is not strictly necessary; Nakao used a collection tank machined in a large piece of thermally conductive metal and measured the temperature of the metal instead of a water bath temperature [7]. The

* We use P_{meas} and $T_{\text{H}_2\text{O}}$ to calculate density in Equation 1. In other circumstances, one would choose to use corrected pressure and temperature values ($P_{\text{meas}} - P_{\text{err}}$ and $T_{\text{H}_2\text{O}} - T_{\text{err}}$) instead.

pressure sensors should be connected directly to the tank, not to the piping carrying the flow to the tank or any place where they are subject to flow (and pressure) dependent pressure drops.

Correlated pressure uncertainties (e.g., a zero offset in calibration) do not contribute to RoR flow uncertainty, but gain errors or non-linearity of pressure sensors are a concern. Using the RoR system over a wider range of pressures reduces the uncertainty related to both pressure and temperature measurement. This can be done by increasing the fill time or reducing the collection volume. Therefore, a well-designed RoR standard has a collection tank that is small enough to produce large pressure changes in a short collection time, but has large surface area to improve heat transfer. NIST intends to build a new RoR standard to measure flows from 0.01 sccm to 1 sccm using a 0.3 L collection tank and fittings with low leak rates.

In this work, we benefited from having a validated *PVTt* standard to use as a reference to assess RoR flow and temperature measurements. But one can assess temperature corrections for flow work to a RoR standard without implementing *PVTt* measurements. The temperature of the gas at the end of a fill can be calculated using data like those in Figure 2 ($T = T_{\text{H}_2\text{O}} P^{(f)} / P_{\text{eq}}^{(f)}$). Temperature errors can be tabulated as a function of flow and an empirical correction applied to $T_{\text{H}_2\text{O}}$ to improve flow measurements at high flows where temperature errors are a large uncertainty source. The uncertainty analysis for this approach would need to include the uncertainty of the corrections. In lieu of making corrections, one can use a collection tank with greater heat transfer to the surroundings ($>hA$) to reduce T_{err} to small values.

The comparison of RoR and *PVTt* data revealed that there are transient effects, apparently related to the in-rush of gas at the beginning of a collection, that last much longer than the expected response time of the sensors to pressure changes. We speculate that the long transients are related to the internal temperature of the pressure transducers. Sensors don't necessarily behave with a first order time response and a single time constant. A pressure sensor exposed to a step change in pressure may have a short first-order time response of large magnitude for electrical or mechanical reasons, but also have a longer second-order response of small magnitude for thermal reasons. The transient response had opposite signs for the two types of pressure sensors we used, but both types performed well in later portions of a fill ($P > 20$ kPa). These problems can be avoided by making plots like Figure 9 (using the RoR data over the full available pressure range instead of *PVTt* data) and only using results that indicate that steady state has been attained.

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9. Appendix: Derivation of the Temperature Error Due to Flow Work (Equation 9)

Assuming 1) the thermodynamic properties of the gas are uniform in the control volume defined by the tank internal walls (a "lumped parameter analysis"), 2) there is no work other than flow work applied, 3) energy is conserved, and 4) the gas is ideal and has constant specific heat, Equation 11 of reference [6] with heat transfer gives:

$$c_V m \frac{dT}{dt} + c_V T \frac{dm}{dt} = \dot{m} c_P T_{in} - hA(T - T_s) , \quad (A1)$$

where T is the temperature of the gas in the collection tank, T_{in} is the temperature of the gas entering the tank, T_s is the temperature of the surface of the tank, m is the mass of gas in the tank at time t , $\dot{m} = dm/dt$ is the mass flow of gas entering the tank, c_V and c_P are the gas constant volume and constant pressure specific heat capacities respectively, h is the convective heat transfer coefficient between the gas and the tank walls, and A is the surface area of the tank walls. Equation A1 can be rewritten as:

$$c_V m \frac{d(T-T_s)}{dt} + c_V (T - T_s) \frac{dm}{dt} + hA(T - T_s) = \dot{m} c_P T_{in} - c_V \frac{dm}{dt} T_s . \quad (A2)$$

If mass flow $\dot{m}$ is diverted into the tank at $t = 0$,

$$m(t) = m^{(i)} + \dot{m} t , \quad (A3)$$

and this expression can be substituted into Equation A2 to give:

$$c_V [\dot{m} t + m^{(i)}] \frac{d(T-T_s)}{dt} + [c_V \dot{m} + hA](T - T_s) = \dot{m} [c_P T_{in} - c_V T_s] . \quad (A4)$$

Dividing by c_V results in:

$$[\dot{m} t + m^{(i)}] \frac{d(T-T_s)}{dt} + \left[\dot{m} + \frac{hA}{c_V} \right] (T - T_s) = \dot{m} [T_{in} \gamma - T_s] , \quad (A5)$$

where $\gamma = c_P/c_V$. Introducing the dimensionless variables $\hat{t} = t/t^{(f)}$, $\hat{T}_{in} = T_{in}/T_s$, $\hat{\theta} = (T - T_s)/T_s$, and $\Gamma = \frac{hA}{c_V \dot{m}}$ transforms Equation A5 to:

$$\left[\hat{t} + \frac{m^{(i)}}{\dot{m} t^{(f)}} \right] \frac{d\hat{\theta}}{d\hat{t}} + [1 + \Gamma] \hat{\theta} = \hat{T}_{in} \gamma - 1 , \quad (A6)$$

which for the boundary condition $T = T_s$ at $t = 0$ (i.e. $\hat{\theta}(0) = 0$) has the solution:

$$\hat{\theta} = \left(\frac{\hat{T}_{in} \gamma - 1}{1 + \Gamma} \right) \left[1 - \left(\frac{\dot{m} t^{(f)}}{m^{(i)}} \hat{t} + 1 \right)^{-(1+\Gamma)} \right] , \quad (A7)$$

for $\hat{t} < 1$. Converting back to the dimensional variables and assuming that the surface temperature of the tank equals the water bath temperature $T_s = T_{H_2O}$ gives:

$$T_{err} = T - T_{H_2O} = T_{H_2O} \left[\frac{(T_{in}/T_{H_2O})^{\gamma-1}}{1 + \Gamma} \right] \left[1 - \left(\frac{\dot{m} t}{m^{(i)}} + 1 \right)^{-(1+\Gamma)} \right] . \quad (A8)$$

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- [1] Lemmon, E. W., Huber, M. L., and McLinden, M. O., *Refprop 23: Reference Fluid Thermodynamic and Transport Properties*, NIST Standard Reference Database 23, Version 9, National Institute of Standards and Technology, Boulder, CO, November, 2010.
- [2] Coleman, H. W., and Steele, W. G., *Experimentation, Validation, and Uncertainty Analysis for Engineers*, 3rd edition, A. John Wiley and Sons, 2009, Appendix E.
- [3] *Method for Vacuum Leak Calibration*, American Vacuum Society, AVS Standard 2.2-1968, Vac. Sci. Tech., Vol. 5, pp. 219-222, 1968.
- [4] Wright, J. D., Johnson, A. N., Moldover, M. R., and Kline, G. M., *Gas Flowmeter Calibrations with the 34 L and 677 L PVTt Standards*, NIST Special Publication 250-63, National Institute of Standards and Technology, Gaithersburg, Maryland, November 18, 2010, <http://nvlpubs.nist.gov/nistpubs/Legacy/SP/nistspecialpublication250-63.pdf>.
- [5] Wright, J. D. and Johnson, A. N., *NIST Lowers Gas Flow Uncertainties to 0.025 % or Less*, NCSL International Measure, 5, pp. 30 to 39, March, 2010, http://ws680.nist.gov/publication/get_pdf.cfm?pub_id=901413.
- [6] Wright, J. D. and Johnson, A. N., *Uncertainty in Primary Gas Flow Standards Due to Flow Work Phenomena*, FLOMEKO, Salvador, Brazil 2000, https://www.nist.gov/sites/default/files/documents/calibrations/flomeko_2000.pdf.
- [7] Nakao, S.-I., *Development of the PVTt System for Very Low Gas Flow Rates*, Flow Measurement and Instrumentation, 17, pp. 193 to 200, 2006.