

UNCERTAINTY IN PRIMARY GAS FLOW STANDARDS DUE TO FLOW WORK PHENOMENA

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Abstract: Static gravimetric and static volumetric gas flow standards are both affected by uncertainty components related to the measurement of the change of mass of gas within the inventory volume. In the process of diverting gas into the collection vessel, rapid pressure and temperature changes occur in the inventory volume. A low uncertainty gas flow standard requires thorough understanding of these transients so that appropriate instrumentation, system design, and operating procedures may be developed. A thermodynamic model for the flow work phenomena is presented and compared to experimental measurements and strategies for minimizing their effects on flow uncertainty are discussed.

Keywords: primary gas flow standard, flow work, inventory volume, uncertainty, gas flow calibration, diverter valves

1 INTRODUCTION

Meter manufacturers and users employ laboratories with primary flow standards for the calibration of their working flowmeter standards. Such laboratory standards are designed to have the lowest practical measurement uncertainty so that this high accuracy can be passed on to the flowmeter being calibrated and subsequently to the flowmeter application. Presently, the uncertainty of laboratory standards is typically less than 0.2% with a 95% level of confidence. Two commonly used types of primary flow standards are the static gravimetric and static volumetric systems.

In a *static gravimetric* gas flow standard, diverter valves are used to direct flow exiting the meter under test into a collection vessel for a measured time interval. The change in mass in the collection vessel is measured with a weigh scale and divided by the collection time to obtain the mass flow of gas. Generally, there are two additional, smaller inventory volumes in the system where mass changes must be considered as well (see Figure 1). The first of these volumes is bounded by a critical flow venturi (or some other pressure isolation device) on the upstream side, and by the diverter valves on the downstream side. The second of these volumes is bounded by one of the diverter valves on the upstream side, and by an isolation valve on the downstream side (which allows the tank to be disconnected and placed on the weigh scale). The basis equation for mass flow in the static gravimetric flow standard is:

$$\dot{m} = \frac{(m_T^f - m_T^i) + (m_I^f - m_I^i) + (m_{I2}^f - m_{I2}^i)}{\Delta t} \quad (1)$$

where m represents mass, the subscripts T , I , and $I2$ refer to the tank, first inventory volume, and second inventory volume respectively, the superscripts i and f represent initial and final values respectively, and Δt is the collection time. An additional term which accounts for mass changes in the volume between the meter under test and the pressure isolation device (“storage effects”) is sometimes included in Equation 1 for uncertainty analysis purposes, but has been left out here for simplicity. The mass of gas in the two inventory volumes is determined volumetrically, *i.e.* measurements of pressure and temperature in each volume (ideally, spatial averages), measured at the start and stop times, are converted to gas density with an equation of state, and then multiplied by the size of each inventory volume,

$$m_I = \rho_I(P_I, T_I) \cdot V_I \quad \text{and} \quad m_{I2} = \rho_{I2}(P_{I2}, T_{I2}) \cdot V_{I2} \quad (2)$$

When Equation 2 is substituted into Equation 1, the gravimetric basis equation becomes,

$$\dot{m} = \frac{(m_T^f - m_T^i) + (\rho_1^f - \rho_1^i) \cdot V_1 + (\rho_{I2}^f - \rho_{I2}^i) \cdot V_{I2}}{\Delta t} \quad (3)$$

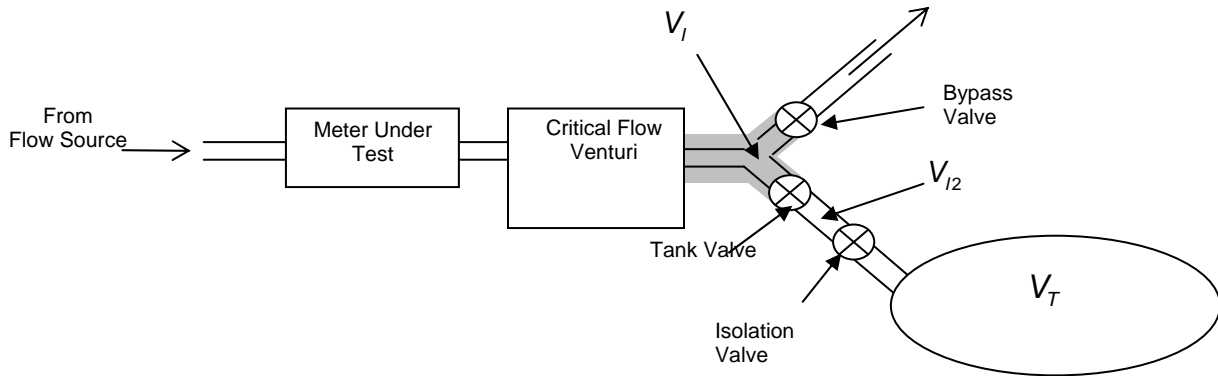


Figure 1. A schematic diagram of a static gravimetric gas flow standard. The collection tank volume is disconnected at the isolation valve for placement on a weigh scale.

A *static volumetric* gas flow standard or pressure-volume-temperature-time (PVTt) system is shown in Figure 2. This type of device differs from the gravimetric standard in that the mass change of gas in the collection tank is based on initial and final pressure and temperature measurements made in the tank (spatial averages) along with the tank volume, not on a weigh scale. Since the collection tank remains connected at all times, the system does not need an isolation valve and hence only a single inventory volume, V_I , needs to be considered. The basis equation is:

$$\dot{m} = \frac{V_T \cdot (\rho_T^f - \rho_T^i) + V_I \cdot (\rho_1^f - \rho_1^i)}{\Delta t} \quad (4)$$

In both types of systems, the pressure isolation device may be a critical flow venturi or a back-pressure regulator. The pressure isolation device is necessary to maintain stable temperature and pressure conditions at the test section. It isolates the meter under test from the extreme pressure variations that occur downstream due to the operation of the diverter valves and the rising pressure of the filling collection tank.

Within the flow metrology community, there is a continuous effort to reduce the uncertainty of primary gas flow standards. Published uncertainty analyses for static gravimetric facilities quote uncertainties of 0.01% to 0.25% [1, 2, 3, 4, 5] while uncertainties quoted for static volumetric facilities vary between 0.05 % and 0.25% [6, 7, 8]. Further reductions in the uncertainty of static gravimetric and static volumetric gas flow standards require greater understanding of the dynamic behavior of the inventory volumes so that the best designs and methods of operation can be developed.

In this paper, a thermodynamic model for the inventory volume during the flow diversion assuming uniform gas properties and no heat transfer will be discussed. The model gives an estimation of the temporal changes in temperature and pressure in the inventory volume. The effects of instrumentation time constants on the pressure and temperature measurements will be incorporated into the model. Therefore, the model provides a way to estimate uncertainties caused by slow sensors. The model will be compared to experimental data and then used to examine the uncertainty in a primary flow standard caused by slow sensors in the inventory volume.

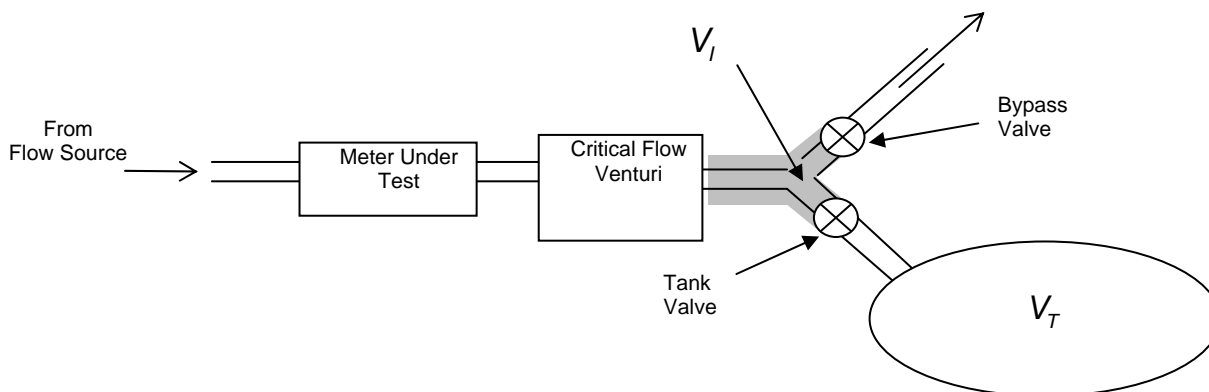


Figure 2. A schematic diagram of a static volumetric or PVTt gas flow standard. The mass of gas in the collection tank is calculated from the tank volume and measurements of pressure and temperature in the tank.

2 QUALITATIVE DESCRIPTION OF INVENTORY VOLUME PHENOMENA

The two types of primary standards described above have the common feature of inventory volumes in which density changes are measured as part of the flow determination. In the gravimetric standard, the pressure and temperature measurements in V_{I2} can be collected in a static manner *i.e.* the user can wait (both before and after the gas collection) for conditions to equilibrate. However, for both the gravimetric and volumetric standards, the pressure and temperature measurements made in the inventory volume V_I in Figures 1 and 2 are made during rapidly changing conditions as flow is diverted. For the remainder of this article, attention will be focused on the dynamics of this inventory volume (V_I) but the inventory volume bounded by the isolation valve in the gravimetric standard (V_{I2}) will not be discussed.

The bypass and tank valves can be operated with *non-zero valve overlap* (*i.e.* where one valve begins to open before the other is fully closed), or with *zero overlap* (where the bypass valve is completely closed before the other begins to open) [9]. With zero overlap, there is no question about lost or extra mass occurring during the diversion. For instance, if the tank is at an initial pressure less than atmospheric, when both valves are partially open, flow can enter the tank from the room instead of through the meter under test. Quantifying the uncertainties related to such flow paths is a daunting task, since they are likely dependent on the flow and various pressure conditions. A zero overlap diverter avoids these difficulties. However, for a zero overlap diverter, there is a short period of time (generally only a fraction of a second) during the actuation of the diverter valves during which both valves are fully closed (the “dead end” time). During the dead end time, the mass of gas that passed through the pressure isolation device accumulates in the inventory volume. The mass accumulation leads to a pressure and temperature rise in the inventory volume. The upper pressure attained in the inventory volume will depend on the mass flow, the size of the inventory volume, the dead end time of the diverter valves, conduit geometry, and heat losses to the surroundings. The pressure in the inventory volume must not be permitted to reach a high enough level that the flow at the venturi is no longer critical, lest a pressure perturbation reach the meter under test and disrupt the steady state flow conditions at the meter. Hence it is important that the diverter valve design be fast acting in a zero overlap system.

It should be noted that although the diverter valves have been described on the basis that there are separate bypass and tank valves, the same concerns apply to flow standards with three-way diverter valves. Some three-way valves have intermediate positions which correspond to the non-zero overlap condition, and those with zero overlap will have finite dead end times. Also, in a system with a bypass valve and a tank valve, switching signals can be delivered to both valves (with the appropriate delay between the signals) so that there is a minimal dead-end time, even for large, slow moving valves.

For a zero overlap diverter, the instant that the bypass valve first reaches the fully closed position, is the time after which all of the mass flowing through the meter under test remains in the system defined by the inventory and tank volumes. Prior to this instant, some of the flow is still exiting the control volume via

the bypass valve. Any time during the start dead end interval (*i.e.* the dead end time that occurs at the start of a collection) could be used as the start time for the flow collection as long as the initial inventory pressure and temperature values are acquired at the same time as that used for the start time. The time at which the bypass valve first reaches the fully closed position is a convenient choice if a trigger signal is available. At the completion of a collection, as before, any time during the stop dead end period is acceptable, but the time that the tank valve first reaches fully closed is often chosen for convenience.

A qualitative examination of the net mass flow and pressure for the inventory volume during flow diversion is shown in Figure 3. Initially, the net mass flow into the inventory volume is zero since the same amount of mass enters through the upstream boundary and leaves through the bypass outlet. The vertical line labeled “A” in Figure 3 represents the time at which the bypass valve begins closing. As the valve closes, flow to the bypass outlet becomes increasingly obstructed, resulting in increasing values of net mass flow and pressure in the inventory. Vertical line “B” represents the time at which the bypass valve is first fully closed, and “C” represents the time when the tank valve begins opening. The time between B and C is the dead end interval when the net mass flow matches the mass flow through the meter under test, and the pressure rises most rapidly. Once the tank valve opens, mass from the pressurized inventory rapidly flows to the evacuated tank, the inventory pressure suddenly falls to the tank pressure, and the inventory net mass flow actually is negative (flow into the tank exceeds the flow from the meter under test). Although a temperature trace is not shown in Figure 3, “flow work” and kinetic energy input cause the temperature to rise as mass accumulates in the inventory volume. Analogous pressure and temperature phenomena occur for the flow diversion at the end of a flow collection. Pressure and temperature instrumentation with poor time response may lead to significant uncertainties when subjected to the rapidly changing thermodynamic conditions in the inventory volume. On the other hand, fast response sensors may allow a single apparatus to be used over a wider flow range. In the following section, a thermodynamic model for predicting the behavior of pressure and temperature in the inventory volume during the flow diversion will be developed.

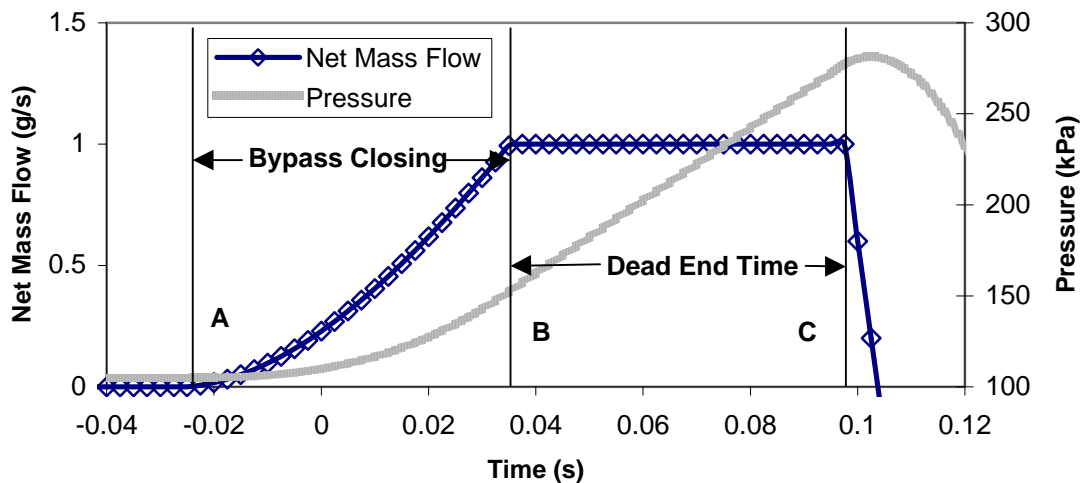


Figure 3. Qualitative plot of net mass flow and pressure in the inventory volume during the start time flow diversion.

3 THERMODYNAMIC MODEL OF THE INVENTORY VOLUME

The temperature and pressure in the inventory volume can be predicted by using the first law of thermodynamics for a stationary control volume,

$$-\iint_S \left(E + \frac{P}{\rho} \right) \rho \vec{v} \cdot \vec{n} dS = \frac{d}{dt} \iiint_V \rho E dV + q_{out} + w_{out}, \quad (5)$$

which states that the net flux of energy across the control volume surface, S , is balanced by the rate of change of the total energy in the control volume, V , plus any heat losses and work (other than flow work) output. In our case, the control volume is the inventory volume between the pressure isolation device and the diverter valves (shaded gray in Figures 1 and 2). The heat term will represent heat losses from the inventory volume to the surroundings. The quantity P/ρ in the surface integral is known as the “flow work”. Flow work is work necessary to push additional gas into an already pressurized volume, *i.e.* work associated with the pressure at the inlet or outlet of a control volume [10]. As will be seen, the input of flow work and kinetic energy by the incoming gas may lead to rapidly increasing temperatures in the inventory volume during the dead end time.

If the thermodynamic properties are assumed uniform in the control volume and on the control surface (a “lumped parameter analysis”), and there is no work other than flow work applied to the system, Equation 5 can be simplified to,

$$\left[E + \frac{P}{\rho} \right]_{in} \dot{m}_{in} - \left[E + \frac{P}{\rho} \right]_{out} \dot{m}_{out} = \frac{d}{dt} [E m(t)]_V + q_{out}, \quad (6)$$

where $m(t)$ is the mass of gas held within the control volume at any particular time, and \dot{m}_{in} and \dot{m}_{out} are the mass flow entering and leaving the control volume respectively. Using the definition of total energy, which equals the gas specific internal energy, u , plus its kinetic and potential energies, Equation 6 expands to:

$$\left[u + \frac{P}{\rho} + KE + PE \right]_{in} \dot{m}_{in} - \left[u + \frac{P}{\rho} + KE + PE \right]_{out} \dot{m}_{out} = \frac{d}{dt} [(u + KE + PE) m(t)]_V + q_{out}. \quad (7)$$

Next, one can assume that the kinetic and potential energies in the flow leaving the control volume as well as the potential energy of the incoming flow are all negligible. Further, we can make substitutions using the enthalpy which enters and exits the inventory volume:

$$h_{in} = \left[u + \frac{P}{\rho} + KE \right]_{in} \approx C_p T_{in}, \text{ and} \quad (8)$$

$$h_{out} = \left[u + \frac{P}{\rho} \right]_{out} \approx C_p T(t), \quad (9)$$

where C_p is the constant pressure specific heat, and T_{in} is the inlet flow stagnation temperature. The kinetic energy of the inlet flow has been incorporated in h_{in} by using the inlet stagnation temperature. Assuming an ideal gas with constant specific heat, the internal energy is $u = C_v T(t)$, where C_v is the constant volume specific heat. Also, the mass contained within the control volume at any given time is:

$$m(t) = m(0) + \int_0^t \dot{m}_{net} d\tilde{t}, \quad (10)$$

where $\dot{m}_{net} = \dot{m}_{in} - \dot{m}_{out}$ and $m(0)$ is the mass in the control volume at the steady state condition just before the flow diversion is initiated. The problem can be simplified by assuming the system is adiabatic ($q_{out} = 0$). The lack of a heat loss term will cause over predictions of the inventory temperature and is a more conservative approach in terms of calculating temperature measurement uncertainties.

Making the substitutions given above into Equation 7 leads to the following differential equation for the temperature in the inventory volume:

$$\frac{dT}{dt} = \frac{C_p T_{in} \dot{m}_{in} - C_p T(t) \dot{m}_{out} - C_V T(t) \dot{m}_{net}}{C_V \left[m(0) + \int_0^t \dot{m}_{net} d\tilde{t} \right]} \quad (11)$$

Equation 11 can be solved by standard numerical techniques applied to ordinary differential equations (such as the Runge-Kutta method) to yield temperature in the inventory volume.

Using the temperature calculated in Equation 11, the ideal gas law, and conservation of mass, one can calculate the pressure in the inventory as a function of time via the following expression:

$$P(t) = \frac{\left[m(0) + \int_0^t \dot{m}_{net} d\tilde{t} \right] R T(t)}{V_i}, \quad (12)$$

where R is the gas constant, *i.e.* the universal gas constant divided by the gas molecular weight.

Equations 11 and 12 allow one to predict the inventory temperature and pressure during the start and stop flow diversions. Predictions of the temperature and pressure transients are useful when studying uncertainties related to the inventory volume. The necessary inputs are: the mass flow at the inlet and outlet of the inventory volume as a function of time during the flow diversion, the initial inventory temperature and pressure (*i.e.* at event A in Figure 3), the size of the volume, and certain gas properties (specific heats, molecular weight, etc.).

4 TIME RESPONSE OF INVENTORY SENSORS

The fast pressure and temperature transients in the inventory volume may not be observed at all unless quick response, high time resolution sensors and data acquisition systems are used. Valve actuation times of 50 ms or less are common in primary gas flow standards. But a typical sheathed thermister will have a time constant on the order of 10 s. With such a disparity of time scales, the inventory temperature transients would not be detected.

In order to predict the output of a real temperature sensor when exposed to the inventory volume transients, the temperature calculated via Equation 11 can be used as the true temperature, $T(t)$, and a first order response equation [11] can be used to calculate the temperature sensor output, T_{sens} :

$$T_{sens} = T(0) \cdot e^{-t/\tau} + \frac{1}{\tau} \cdot e^{-t/\tau} \int_0^t T(\tilde{t}) e^{\tilde{t}/\tau} d\tilde{t}, \quad (13)$$

where τ is the sensor time constant. Due to the functional form of the integrand in Equation 13, it must be evaluated numerically. An analogous approach can be applied to the pressure measurements to assess the uncertainties caused by a slow pressure sensor.

5 COMPARISON OF THERMODYNAMIC MODEL TO EXPERIMENTAL DATA

At the National Institute of Standards and Technology a small PVTt gas flow standard was used as a testbed to check the theoretical predictions of pressure and temperature in the inventory volume. The inventory volume of the PVTt system is shown in Figure 4. Critical flow venturis with throat diameters between 0.3 mm and 1.1 mm were used at mass flows ranging from 0.03 g/s and 1.0 g/s. Flow was measured with the PVTt system with uncertainty less than 0.1%. The inventory volume was nominally 115 cm³.

The pressure sensor had a response time of 3 ms according to the manufacturer's specification. However, flow restrictions imposed by the pressure tap and the connecting tubing for the pressure sensor can increase the time constant. Therefore, experiments were conducted in situ to measure the time constant of the pressure transducer. In these tests, a balloon was placed over the inlet to the inventory volume and inflated. Time traces of the pressure sensor output were acquired at 3 kHz while the balloon was ruptured and the results were fitted with an exponential response function to obtain the sensor time constant. These tests gave a nominal time constant for the pressure sensor of 8 ms and this value was

used in the predictive model. The measured time constant was larger than the manufacturer's specification as one would expect given the connecting tubing restrictions.

The temperature sensor was a type T thermocouple with wires 0.025 mm in diameter. Prior to installation in the inventory volume, the thermocouple time constant was measured experimentally. A gas flow jet was applied to the thermocouple to approximate the flow conditions to which the thermocouple would be exposed in the inventory volume. A shutter was used to suddenly apply an infrared source on a parabolic mirror with the thermocouple located at the focal point. The temperature readings were acquired at 3 kHz during actuation of the shutter. The thermocouple time constant varied inversely with the gas flow and ranged between 20 ms and 100 ms. The inverse dependence of the time constant on the flow of gas across the thermocouple is as expected based on temperature sensor time constant theory.¹¹ A quadratic function was fitted to the experimental data so that the time constant could be calculated for a postulated mass flow of gas when using the predictive model. Slower response but more accurate pressure and temperature sensors were also installed in the inventory volume for comparison to the fast sensors under steady state conditions.

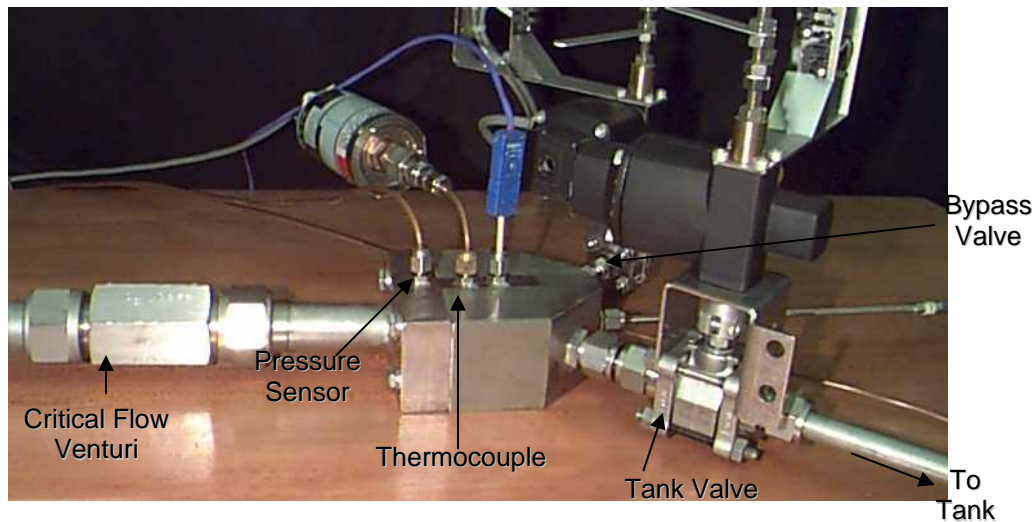


Figure 4. The inventory volume used in the experimental evaluation of the thermodynamic model.

Experimental measurements of the pressure and temperature in the inventory volume are presented in Figures 5 and 6, along with predictions based on the thermodynamic model. Time zero in the plots represents the time that the bypass valve reaches the fully closed position (the beginning of the dead end time). The tank valve opens at the time of approximately 0.1 s and the pressure drops rapidly. Model predictions were calculated only to the end of the dead end time since the collection start and stop time is normally within this interval. For the model, a linear ramp function was used for the mass flow exiting the inventory (lasting 40 ms) to represent the change in flow as the bypass valve is moving closed. As stated before, the experimentally determined time constants for the pressure and temperature sensors were used.

Figure 6 shows the model predictions for a temperature sensor time constant of zero, *i.e.* our estimate of the actual temperature in the inventory volume based on the thermodynamic model, through the dead end time. At higher mass flows, the inventory temperature shows an asymptotic behavior that can be explained via Equation 12: while the increment of enthalpy per time added to the inventory volume remains constant, the mass in the denominator is growing with the passage of time. The asymptotic behavior is somewhat masked in the experimental results by the time constant of the thermocouple.

The thermodynamic model has limitations due to the simplifying assumptions made in its derivation, but the agreement with the experimental measurements is encouraging. The derivation assumed that the gas properties were uniform throughout the inventory volume, yet we know this is not correct. Spatial variations exist, primarily due to the jet of relatively cold gas entering via the critical flow venturi. During the experimental work, some crude temperature profile data were gathered by moving the thermocouple to various insertion depths. For the 0.7 g/s flow, differences of as much as 5% of the absolute

temperature were observed between the centerline and near wall locations, while for the 0.2 g/s flow, the variations observed were 1.3%. The profile data also showed generally decreasing temperatures as the thermocouple was placed closer to the wall. This can be explained by heat transfer from the gas to the inventory wall and/or by longer sensor time constants since the thermocouple is in a lower velocity region.

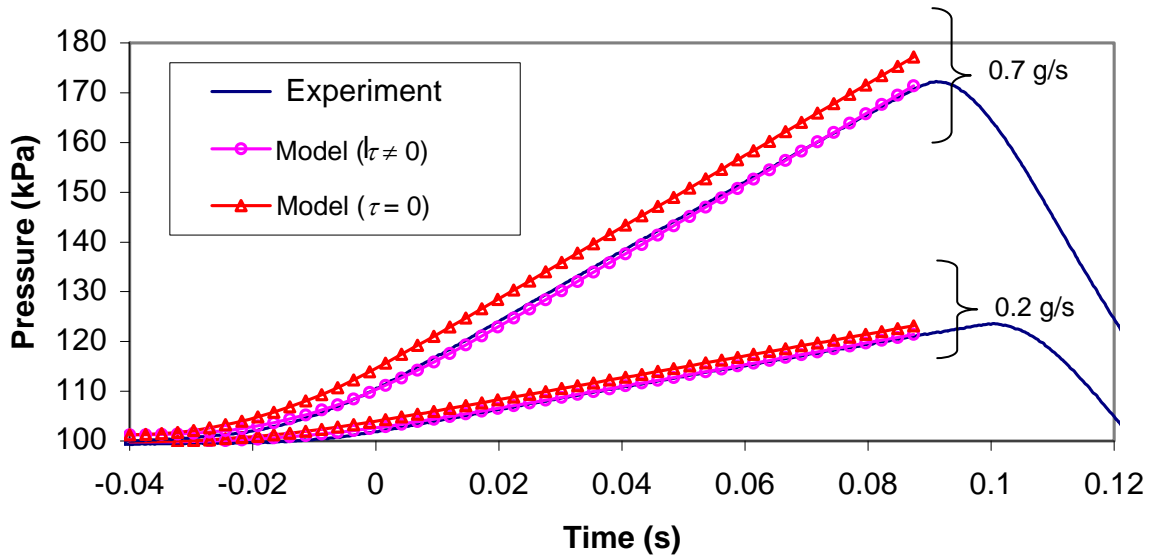


Figure 5. Experimentally measured pressure data and thermodynamic model predictions for mass flows of nominally 0.2 g/s and 0.7 g/s. Model predictions for zero and finite time constants are shown.

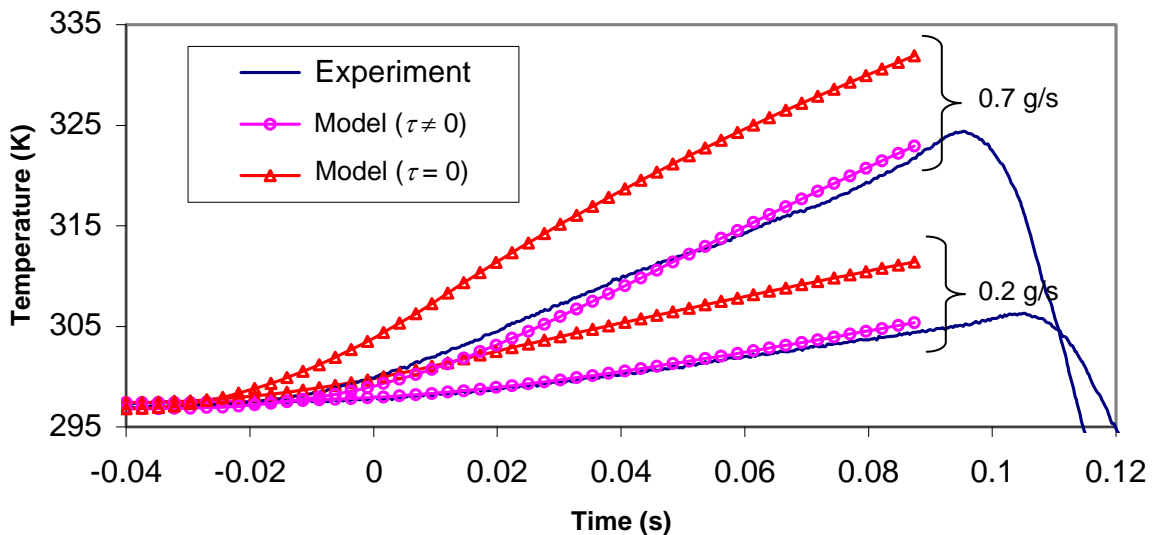


Figure 6. Experimentally measured temperature traces in the inventory volume for flows of nominally 0.2 g/s and 0.7 g/s. Also shown are temperature predictions from the model, with zero and finite temperature sensor time constants.

It was also observed that somewhat random departures between the experimental temperature data and the model became larger for larger mass flows. It is likely that the mixing of the cold jet flow and the hot gas already in the inventory causes the random temperature departures from the model. The spatial non-uniformity of the temperature within the inventory volume is a source of uncertainty which unfortunately is not addressed herein, since computer simulations, or extensive experimental measurements would be required.

The general agreement of the lumped thermodynamic model with the experimental measurements suggests that the model captures the pertinent physics responsible for rapid changes of inventory temperature and pressure. It can be seen from the model that if a start time late in the dead end time were used, and if slow response pressure and temperature sensors were used, significant errors in the measurement of inventory mass would result, particularly at high mass flows. The model can now be incorporated into an uncertainty analysis or used to assess some of the uncertainties related to the inventory volume.

6 UNCERTAINTY OF INVENTORY MASS DUE TO SLOW SENSORS

For the sake of exploring certain test cases, the thermodynamic model of the inventory volume will be used with zero and finite time constants to calculate the uncertainty in pressure and temperature measurements caused by slow sensors. It can be shown that for a static gravimetric or static volumetric gas flow standard, uncertainties in the measurements of the inventory pressure and temperature due to slow time response sensors cause a fractional uncertainty of the mass flow determination of:

$$\frac{Um_i}{m_{total}} = \frac{V_i}{R \cdot m_{total}} \left[\left(\frac{1}{T_i^f} \cdot UP_i^f - \frac{1}{T_i^i} \cdot UP_i^i \right) + \left(\frac{P_i^i}{(T_i^i)^2} \cdot UT_i^i - \frac{P_i^f}{(T_i^f)^2} \cdot UT_i^f \right) \right] \quad (14)$$

where UP_i , UT_i , and Um_i are dimensional uncertainties of the inventory pressure, the inventory temperature, and the inventory mass change during the collection, respectively. The quantity m_{total} is the mass collected in both the tank and in the inventory volume. The uncertainties due to slow pressure and temperature sensors have not been combined by root sum square because they are correlated. The uncertainties in pressure and temperature due to slow sensors will have the same polarity (both quantities will be under-reported due to finite time constants) and their magnitudes are related to each other via the mass flow, the size of the inventory volume, etc.

In the following discussion, Equation 14 will be used to consider design and operational features of a gas flow standard which reduce uncertainties caused by slow sensors in the inventory volume. It is important to note that for the sake of simplicity, many uncertainty components will be neglected in the following discussion, such as sensor calibration uncertainties, spatial non-uniformities, and collection time uncertainties. These components should not be neglected in a complete uncertainty analysis.

Examining Equation 14, if all of the quantities evaluated at initial and final conditions are equal (*i.e.* $UT_i^i = UT_i^f$, $UP_i^i = UP_i^f$, $T_i^i = T_i^f$, and $P_i^i = P_i^f$), then the terms within parentheses cancel, and the flow uncertainty related to the inventory volume is zero. In this special circumstance, even using an incorrect value for the size of the inventory volume (V_i) does no harm. The first two requirements (equal uncertainty in the initial and final pressure and temperature measurements) is very nearly true in the case of "symmetric" diversions. By symmetric diversion we mean that the operation of the valves is such that the net mass flow into the inventory volume (m_{net}) has the same behavior as a function of time, for both the start and stop diversions. For a symmetric system, the pressure and temperature transients will be the same for both the start and stop diversions. Another requirement for a symmetric system is that the time at which the inventory measurements are made is consistent between the start and stop diversions. Under these conditions, the uncertainties in the measurement of the inventory pressure and temperature will be the same for the start and stop diversions.

The third requirement, that the initial and final inventory temperatures be equal ($T_i^i = T_i^f$) is often nearly true as well. However, the flow work phenomenon (both positive and negative) applies to the inventory volume as it quickly empties and then fills during the collection time, so it is common for the final inventory temperature to differ from the initial. For the systems we have tested, the inventory temperature difference between start and stop is generally less than 2 K.

The last requirement for cancellation of uncertainties from the inventory volume is that the initial and final inventory pressures be equal ($P_i^i = P_i^f$). For many systems, this is the hardest requirement to meet. If the bypass valve exhausts flow to the atmosphere, then the condition can be met by making the final tank pressure equal to the barometric pressure. However it is common practice to fill the tank to higher pressures in order to increase the collected mass and lengthen the collection time and thereby reduce pressure sensor or weigh scale and timing uncertainties. In some systems, the source of gas is the atmosphere and the bypass valve allows flow to a vacuum pump. In order to maintain critical flow at the venturi, the tank is filled to nominally 50 kPa. Hence the inventory pressure changes between approximately 0 kPa and 50 kPa.

In cases where the cancellation of terms in Equation 14 cannot be easily accomplished, uncertainties related to the inventory volume can be forced to a negligible level by designing and operating the flow standard so that the mass of gas collected in the tank is large relative to the mass collected in the inventory, *i.e.* $m_T \gg m_i$ or $V_T \gg V_i$. A design rule of thumb is that the ratio of tank volume to inventory volume should be 1000 or greater.

To explore inventory related uncertainties further, consider a system which has a tank volume of 100000 cm³, an inventory volume of 100 cm³ ($V_T/V_i = 1000$), with the same diverter valve, timing trigger operation, and instrumentation described in the experimental section of this article. The uncertainties due to slow sensors in inventory temperature and pressure at a flow of 0.70 g/s can be estimated via the model calculations (see Figures 5 and 6) as 3 K and 4 kPa respectively. Inventory time traces have been studied to show that the diverter valves act symmetrically, hence initial and final uncertainties in the pressure and temperature measurements are assumed equal. Start and stop tank pressures of 5 kPa and 200 kPa will be used, and the start inventory pressure is 100 kPa. The change in the inventory temperature will be assumed to be 0.5 K. For these conditions, the inventory related uncertainties amount to only 0.0005%.

To demonstrate a case where inventory uncertainties are more important, consider a system with a tank volume of 10000 cm³ and an inventory volume of 100 cm³ ($V_T/V_i = 100$). As in the prior example, the start and stop tank pressures of 5 kPa and 200 kPa, a start inventory pressure of 100 kPa, and the inventory temperature change of 0.5 K will be used. It will be assumed that the valve operation is symmetric again. Assume the same flow of 0.70 g/s, but now the inventory sensors have such long time constants that they do not sense the pressure and temperature transients at all. Also, assume that a start and stop time near the end of the dead end times are used, leading to uncertainties of 34 K and 75 kPa in temperature and pressure for both the start and stop diversions. For these conditions, the inventory related uncertainties are 0.059%. For this case, although the uncertainties in the sensor measurements are the same for the start and stop diversions, the difference in magnitude of the sensitivity coefficients (particularly because of inventory pressure) prevents uncertainty cancellation. If the stop pressure is chosen to be 100 kPa instead of 200 kPa, the inventory uncertainties drop to 0.0009% due to the cancellation effect. For a symmetric system, stopping the collection so that the initial and final inventory pressures are the same reduces the uncertainty.

A case with asymmetric valve behavior can lead to very large inventory uncertainties. Let's modify the last case which had slow inventory sensors, $V_T/V_i = 100$, and a stop pressure of 100 kPa. Suppose that the start time is the time at which the bypass valve first reaches fully closed (the beginning of the start dead end time). The uncertainty in the initial inventory measurements is 14 kPa and 7 K based on the model. Suppose that the stop time is taken as the time at which the bypass valve first begins to open at the end of the collection (the end of the stop dead end time). This gives uncertainties in the final inventory measurements of 75 kPa and 34 K. This case leads to inventory uncertainty contributions of 0.546%. In an asymmetric system, a higher stop pressure is sometimes beneficial because it leads to better cancellation of terms in Equation 14. If the stop pressure for this case is set to 200 kPa, the inventory uncertainty contribution drops to 0.206%.

7 CONCLUSIONS

A model for predicting the temperature and pressure transients in the inventory volume of a gas flow standard during flow diversion has been described. The model also allows prediction of uncertainties in temperature and pressure measurements due to insufficiently fast sensor response. The model has been compared to experimental data, and despite the simplifying assumptions of spatial uniformity and no heat

transfer, the model appears to capture the pertinent physics. The model and experiments demonstrate that quite large temperature and pressure excursions are possible during the dead end time when the diverter valve is temporarily closed to both outlets.

An uncertainty analysis and the thermodynamic model of the inventory volume are valuable for designing gas flow standards and deciding operating procedures that reduce flow uncertainties. It is widely recognized that it is desirable to have fast acting valves, short dead end times, and small inventory volumes with respect to the collection volume in gas flow standards, and these rules of thumb are reinforced by the present work. For instance, designing the system so that the tank volume is 1000 times or more larger than the inventory volume generally reduces inventory uncertainties to a negligible level. Fast acting diverter valves and short dead end times reduce the temperature and pressure transients. Zero overlap operation of the diverter valve is recommended to avoid difficult to estimate mass losses, but the start and stop times should be as early in the dead end time as possible (*i.e.* at the first closure of the bypass valve and tank valve respectively) to reduce uncertainties due to slow response inventory sensors. If the system has symmetric diverter valves, operating the system so that the inventory start and stop pressures are equal leads to cancellation of uncertainties in Equation 14 and dramatically reduces inventory uncertainties.

Finally, it should be noted that in this study, adiabatic conditions, as well as spatially uniform temperature and pressure within the inventory volume have been assumed and this is certainly not the case in reality. The issue of how heat transfer and spatial variations contribute to the flow measurement uncertainty requires further study, probably by computer simulation.

8 ACKNOWLEDGEMENTS

The authors wish to acknowledge Peter I. Rothfleisch for his ideas and invaluable assistance in both the thermodynamic and experimental areas of this paper.

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