

Hydrogen Field Test Standard: Laboratory Performance

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Abstract

The National Institute of Standards and Technology (NIST) developed a prototype field test standard (FTS) that incorporates three test methods that could be used by state weights and measures inspectors to periodically test retail hydrogen dispensers, much as gasoline dispensers are tested today. The three field test methods are: 1) gravimetric, 2) Pressure, Volume, Temperature (*PVT*), and 3) master meter. The FTS was tested in NIST's Transient Flow Facility with helium gas. All three methods agree within the expected uncertainty of 0.57 % for all test drafts of helium gas in the laboratory setting. The time required to perform six test drafts is similar for all three methods, ranging from 5.8 h for the gravimetric method to 7.5 h for the *PVT* method. The estimated cost of equipment to perform each method ranges from \$18K (*PVT* method) to \$29K (master meter method).

The laboratory tests show that 1) it is critical to wait for thermal equilibrium to achieve density measurements in the FTS that meet the desired uncertainty requirements for the *PVT* and master meter methods and 2) buoyancy corrections are important for the lowest uncertainty gravimetric measurements.

The wait time for thermal equilibrium following a fill or blow-down of the FTS tank will depend on the temperature difference between the atmosphere and the gas collected in the FTS. In general, we found a wait time of 20 min introduces errors < 0.1 % and < 0.04 % in the *PVT* and master meter methods, respectively. However, this is only valid for the master meter method if the starting pressure (pre-fill condition) is within 173 kPa of the ending (post blow-down condition) pressure. This wait time increases to 1.5 hours if the pressure change is as large as 690 kPa.

The importance of buoyancy corrections increases as the atmospheric air density increases from the conventional value of 1.2 kg/m³, the default value used by the scale manufacturer. Atmospheric temperature, pressure, and relative humidity changes can be expected during a test draft, thus the buoyancy correction is different when the tank is weighed "full" from that when it was weighed "empty". For example, if gravimetric measurements were made in Anchorage, Alaska (where the air density is typically 6.9 % higher than the conventional value) and the temperature changed by 5 K, the relative humidity by 3 %, and the atmospheric pressure by 300 Pa between weighing of the empty and full FTS, an error of 0.12 % would result if the changes were ignored.

1. Introduction

Demonstration vehicles are refueled with hydrogen (H₂) from dispensers within 3 to 5 minutes using sequential gas releases from a bank of pressurized cylinders. The sequential releases generate large, rapidly-changing, gas flows (0 kg/min to 10 kg/min) spanning a wide pressure range (0 MPa to 70 MPa). Measuring the flow under these rapidly changing temperature, pressure, and flow conditions is difficult, but prior research in our Transient Flow Facility (TFF) shows that Coriolis meters can measure the totalized flow within 1 % under simulated H₂

dispenser conditions [1]. Therefore, it is feasible for well-designed commercial dispensers to meet the proposed international requirement of 1.5 % accuracy for dispensing units [2].

Here, our attention turns to how state weights and measures inspectors will verify the accuracy of dispensers in the field. What will be the analog of the 5 gallon test measures presently used to check gasoline dispensers?

In this work, we tested three methods for field testing H₂ dispensers: 1) **gravimetric**; where the mass dispensed is determined by weighing a tank before and after filling it with H₂, 2) **Pressure, Volume, Temperature (PVT)**; where the mass dispensed into the tank is determined from the tank's internal volume and gas density (ρ) change from before and after filling, and 3) **master meter (MM)**; where the mass dispensed is determined by integrating a well calibrated flow meter's measurements of the H₂ gas being blown-down from the filled tank. This work is being performed in two parts: 1) a laboratory phase and 2) a field phase. An uncertainty analysis is provided for each method. The desired uncertainty is 0.5 %; one third of the proposed requirement of 1.5 % for dispensing units. We constructed a prototype field test standard (FTS) to compare the three methods in terms of cost, ease of use, time efficiency, and uncertainty. The FTS will be used in the laboratory and in the field. All three methods agree within the expected uncertainty of 0.57 % for all test drafts of helium gas in the laboratory setting. Figure 1 shows these results for five test drafts of 0.5 kg, 1 kg, and 1.7 kg He gas.

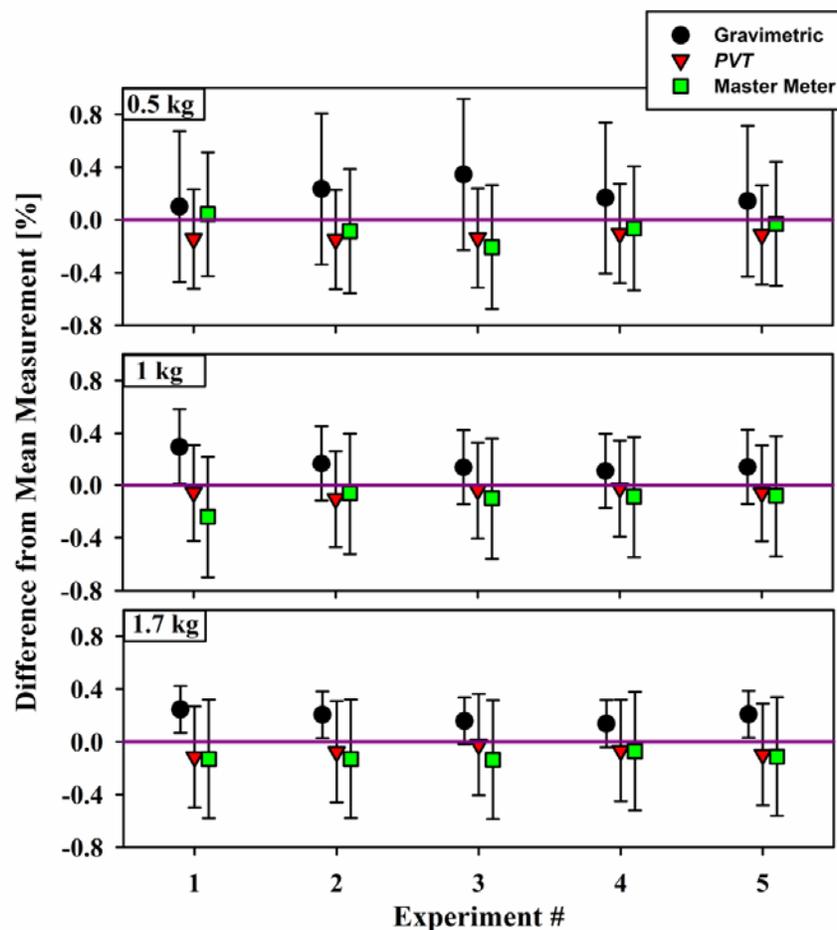


Fig. 1. Agreement of the three test methods for the test draft of 0.5 kg, 1 kg, and 1.7 kg of He gas. The average of all three methods is used as the reference value (difference = 0).

The purpose of the laboratory phase is to design, construct, and test a FTS in a controlled environment, *i.e.*, NIST's Transient Flow Facility (TFF) and using helium (He) as a surrogate gas for H₂. The TFF allows us to: 1) evaluate each field test method without the time constraints that will be encountered in the field, 2) use a more-accurate pressure gauge that is incompatible with explosion hazards in the field, and 3) achieve more reproducible results. The laboratory tests are complete and are presented in this publication.

A field test phase will be carried out at a H₂ dispenser location. The location(s) are yet to be determined. However, the dispenser that will probably be tested pre-cools the H₂ gas to an unknown temperature and has a specified minimum measured quantity (MMQ) of 0.5 kg. The minimum and maximum flows from this dispenser are 30 g/min and 3.6 kg/min respectively. Compared to no pre-cooling (as in the TFF), the pre-cooling of the gas will allow for faster filling times.

2. Experimental Design

2.1 The Field Test Standard

The FTS consists of a 35 MPa (at 15 °C), 1 kg H₂ capacity storage tank that is mounted into a frame made from 2.5 cm² 80/20 extrusion aluminum with wheels for mobility. The storage tank is a type 3 cylinder; a seamless aluminum liner fully wrapped with a continuous filament made of carbon fiber in an epoxy reinforcement laminate [3]. The empty weight of the FTS is approximately 79 kg. Figure 2 shows the FTS in the horizontal position. For density measurements, the FTS is equipped with two, 46 cm long type K thermocouples inserted at each end (to reduce stem conduction errors, thermocouples with a long insertion depth were chosen) and two analog pressure sensors; one with a 35 MPa range and one with a 1.4 MPa range. Accompanying the FTS are 1) a 150 kg weigh scale with 1 g resolution for gravimetric measurements and 2) a portable data acquisition (DAQ) box and laptop with acquisition software. The FTS was designed to be positioned vertically so it fits completely on the scale weighing platform with no wires or plumbing connected to it. The DAQ box supplies power to the master meter and acquires data from the temperature and pressure sensors. All wires can be easily plugged into or unplugged from the DAQ box and coiled on the FTS frame during weighing. Figure 3 shows the FTS on the scale with the accompanying DAQ components. All electrical components installed in and that operate within 5 meters of the FTS are "intrinsically" safe for use with hydrogen.

Elastomer materials are subject to H₂ embrittlement just as metals are [4,5,6], therefore all valves have H₂ compatible seating material. However "compatibility" does not guarantee a specific service life. The inlet and outlet of the FTS have ball check valves that are made completely from stainless steel. All plumbing on the FTS and the diaphragm in the pressure sensors is 316-stainless steel. The thermocouple (TC) sheath material is Inconel¹. It is uncertain what 35 MPa H₂ gas will do to the elastomers in the valves, the Inconel sheath material, and the pressure sensors (leaks past the sensing element into the electronics will cause damage). The valves will be checked for leaks following field tests and the pressure sensor and TC calibrations checked.

¹ 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.

2.2 Laboratory Test Protocol:

The Laboratory tests were carried out to mimic future field tests as closely as possible. The smallest quantity verified is specified by the dispenser manufacturer as the minimum measured quantity (MMQ) and is 0.5 kg for the tests presented here. The maximum quantity is limited by the H₂ storage tank to approximately 1.7 kg He (1 kg H₂) at 34.5 MPa (5000 psi) and 15 °C. NIST Handbook 44 [7] states three consecutive test drafts of approximately the same size of the MMQ and the greater of 10 times the MMQ or 1 kg. We performed five test drafts for the collection of 0.5 kg, 1.0 kg, and 1.7 kg He gas. The small collection tank limited us from testing 10 times the MMQ. A coriolis meter was installed upstream of the FTS tank to aid in delivering the same total mass to the tank to assess the draft-to-draft repeatability (Fig. 4). The pressure and temperature in the tank was monitored continuously during the fill. If the temperature had approached 80 °C (the temperature at which the tank materials will be damaged), the fill would have been halted by the operator [8].

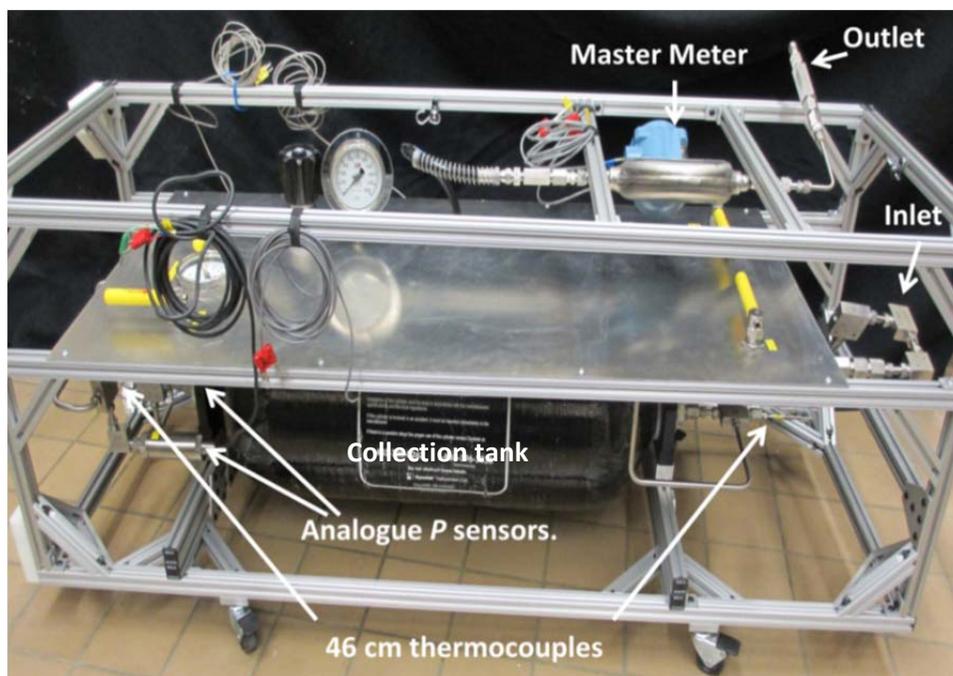


Fig. 2. Portable FTS in horizontal position.

NIST's TFF served as the 35 MPa gas source to fill the FTS. We used flexible compressed natural gas hoses (0.64 cm diameter) that can be easily connected to and disconnected from the FTS to fill the FTS tank and to blow-down the gas into the TFF low pressure tanks. The TFF high capacity compressor re-pressurizes the high pressure tanks so the measurement can be repeated.

Table 1 gives the target mass (m) of gas and the corresponding pressures $P(m)$ at 20 °C that were collected during the laboratory tests and will be collected during the field tests. The expected expanded² uncertainties are included ($k = 2$).

² Expanded uncertainty is the $k = 2$, approximately 95 % uncertainty. Standard uncertainty is the $k = 1$, approximately 68 % uncertainty.

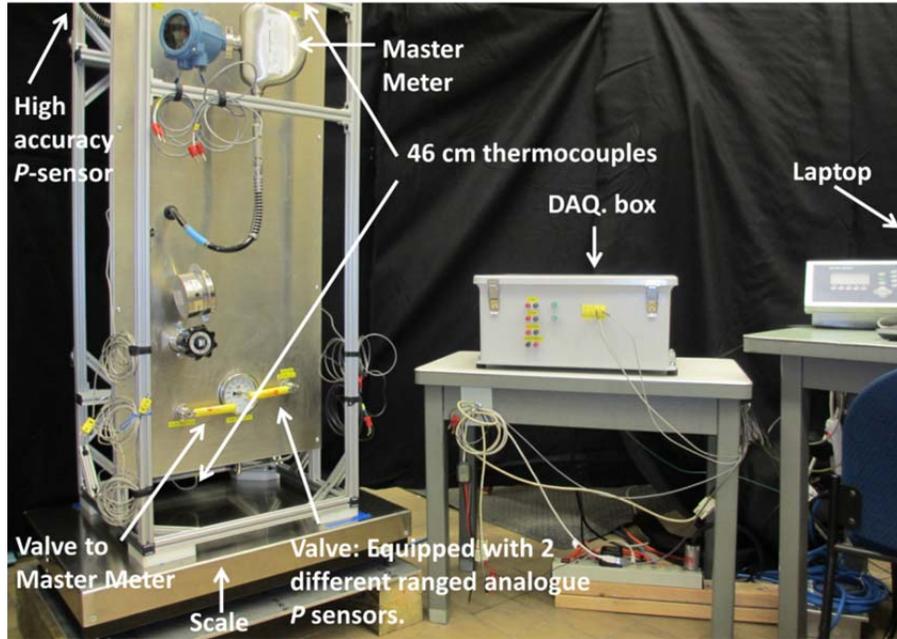


Fig. 3. FTS on the weigh scale with DAQ components.

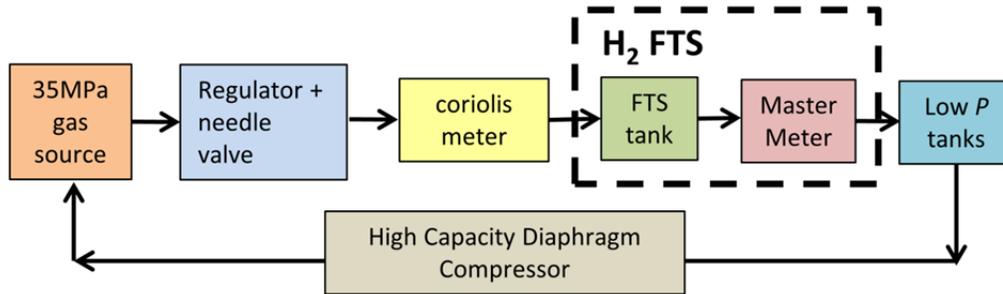


Fig. 4. Schematic of FTS filling and blow-down setup.

Table 1. Target mass (and corresponding pressure) collections for laboratory tests (He) and planned field tests (H₂).

Gas	m [kg]	$P(m)$ [MPa]	Gravimetric U lab (field)	PVT U lab (field)	master meter U lab (field)
He	0.5	8	0.57 (0.57)	0.21 (1.8)	0.45 (0.45)
H ₂	0.5	17	0.57 (0.57)	0.22 (1.7)	0.45 (0.45)
He	1	17	0.29 (0.29)	0.22 (1.7)	0.46 (0.46)
H ₂	1	35	0.29 (0.29)	0.28 (0.91)	0.46 (0.46)
He	1.7	30	0.17 (NA)	0.25 (NA)	0.47 (NA)

We followed 7 steps to collect mass flow measurements with the FTS by all three methods:

- 1) Weigh the FTS with all sensor wires coiled and attached to the frame as shown in Fig. 3.
- 2) Plug the sensors into the DAQ box and make T and P measurements.
- 3) Connect plumbing from the TFF high P tanks to the FTS inlet and fill the tank to the desired mass. During the fill, T and P measurements are made (Fig. 5).
- 4) Wait for thermal equilibration of the tank and conduct final T and P measurements for a final mass determination for the PVT method.
- 5) Disconnect the inlet plumbing; re-coil all sensor wires and attach them to the FTS frame, and weigh the FTS for a final mass measurement for the gravimetric method.
- 6) Connect the outlet plumbing from the FTS to the TFF low- P tanks and connect the T and P sensors and power for the coriolis master meter. Blow-down the gas through the master meter. The master meter transmitter displays the totalized mass through the meter and therefore automated acquisition is not necessary. However, during the laboratory tests, the manufacturer's software for the master meter monitored the flow in real time (Fig. 6). Data from the software agreed with the transmitter readings within 0.012 %. This option is not available for the field tests because the electronics housing has to be open for the communication cable and the meter is not intrinsically safe in this condition.
- 7) Following the blow-down through the master meter and after T and P equilibrium is reached; measurements are again made to determine the mass left in the tank for the master meter method (Section 4.3).

3. Laboratory Results

3.1 Method Comparison

All three methods performed with the FTS agree within 0.57 %. Figure 1 shows the difference between the three different methods and their average for 0.5 kg, 1 kg, and 1.7 kg He test drafts. The gravimetric method generally reads higher than the PVT and MM methods, on average by 0.28 %. The master meter and the PVT methods use the same measurement for the starting mass in the FTS, therefore, errors in their results are correlated.

3.2 Temperature and Pressure Profiles while Dispensing

The TFF operates like a type-D filling station, *i.e.* there is no pre-cooling of the gas. Therefore, to safely fill our type 3 cylinder, the mass flow was controlled such that the temperature in the tank stayed well below 80 °C (353.15 K), the temperature at which the carbon fiber and epoxy wrapping will start to weaken. Table 2 shows the pressure ramp rate (PRR) table for a type-D dispenser with 35 MPa outlet pressure. The highlighted section demonstrates the PRRs that were allowable in the TFF during out tests at room temperature. The room temperature varied from 10 °C to 30 °C.

The ambient temperature plays a significant role in how fast the FTS tank can be safely filled. Figure 5 shows fill up profiles for the test draft of 1 kg and 1.6 kg helium gas. The room temperature was approximately 16 °C the day the 1 kg draft was collected and 18 °C the day the 1.6 kg draft was collected. The lower room temperature allowed for a larger PRR and a fill time of only 6 minutes. A 1.6 kg draft at the same PRR would require 9.6 minutes. However, because the room temperature was higher, the PRR was lower and a longer fill time of approximately 25 minutes was necessary. The internal temperature of the gas stayed well below 354 K during all collections.

Table 2. PRRs and target fill-to pressure as a function of atmospheric temperature and starting tank pressure. Reproduction of table in SAE J2601, 2010 [8].

D-35		Average Pressure Ramp Rate (APRR) (MPa/min)	Fueling Target Pressure (MPa)								
			Initial Tank Pressure (MPa)								
			2	5	10	15	20	30	35	>35	
Ambient Temperature (°C)	>50	no fueling	no fueling	no fueling	no fueling	no fueling	no fueling	no fueling	no fueling	no fueling	no fueling
	50	0.3	41.2	40.9	40.2	39.4	38.7	37.2	36.4	36.4	no fueling
	45	0.3	40.6	40.1	39.4	38.7	38.1	36.9	36.4	36.4	no fueling
	40	0.5	39.9	39.5	38.8	38.2	37.6	36.7	36.4	36.4	no fueling
	35	0.9	39.3	38.9	38.3	37.7	37.3	36.7	36.3	36.3	no fueling
	30	0.9	38.6	38.2	37.5	37.0	36.6	36.0	35.6	35.6	no fueling
	25	1.3	38.0	37.5	36.9	36.4	36.0	35.4	35.4	no fueling	no fueling
	20	1.8	37.3	36.9	36.3	35.8	35.4	34.8	34.8	no fueling	no fueling
	10	3.4	36.3	35.8	35.2	34.8	34.4	33.4	33.4	no fueling	no fueling
	0	6.4	35.6	35.1	34.5	34.0	33.4	31.9	31.9	no fueling	no fueling
	-10	10.4	35.0	34.5	33.7	33.1	32.3	30.5	30.5	no fueling	no fueling
	-20	15.1	34.3	33.7	32.8	32.0	31.0	31.0	no fueling	no fueling	no fueling
	-30	15.1	33.0	32.4	31.4	30.5	29.4	29.4	no fueling	no fueling	no fueling
	-40	15.1	32.4	31.9	31.0	30.3	29.3	29.3	no fueling	no fueling	no fueling
	<-40	no fueling	no fueling	no fueling	no fueling	no fueling	no fueling	no fueling	no fueling	no fueling	no fueling

3.3 Blow-down Profiles

A regulator is installed between the FTS tank outlet and the coriolis master meter to stabilize flow during the blow-down. Figure 6 shows four typical blow-down profiles from the laboratory tests. The traces show blow-down of 0.5 kg of gas with the regulator fully opened, 1 kg of gas with the regulator set to approximately 2.8 MPa (400 psi), 1.6 kg of gas with the regulator set to approximately 2.1 MPa (300 psi), and 1.6 kg of gas with the regulator set to approximately

1.4 MPa (200 psi). Regardless of which profile was used, the master meter and the average of the *PVT* and gravimetric measurements agreed within 0.36 %.

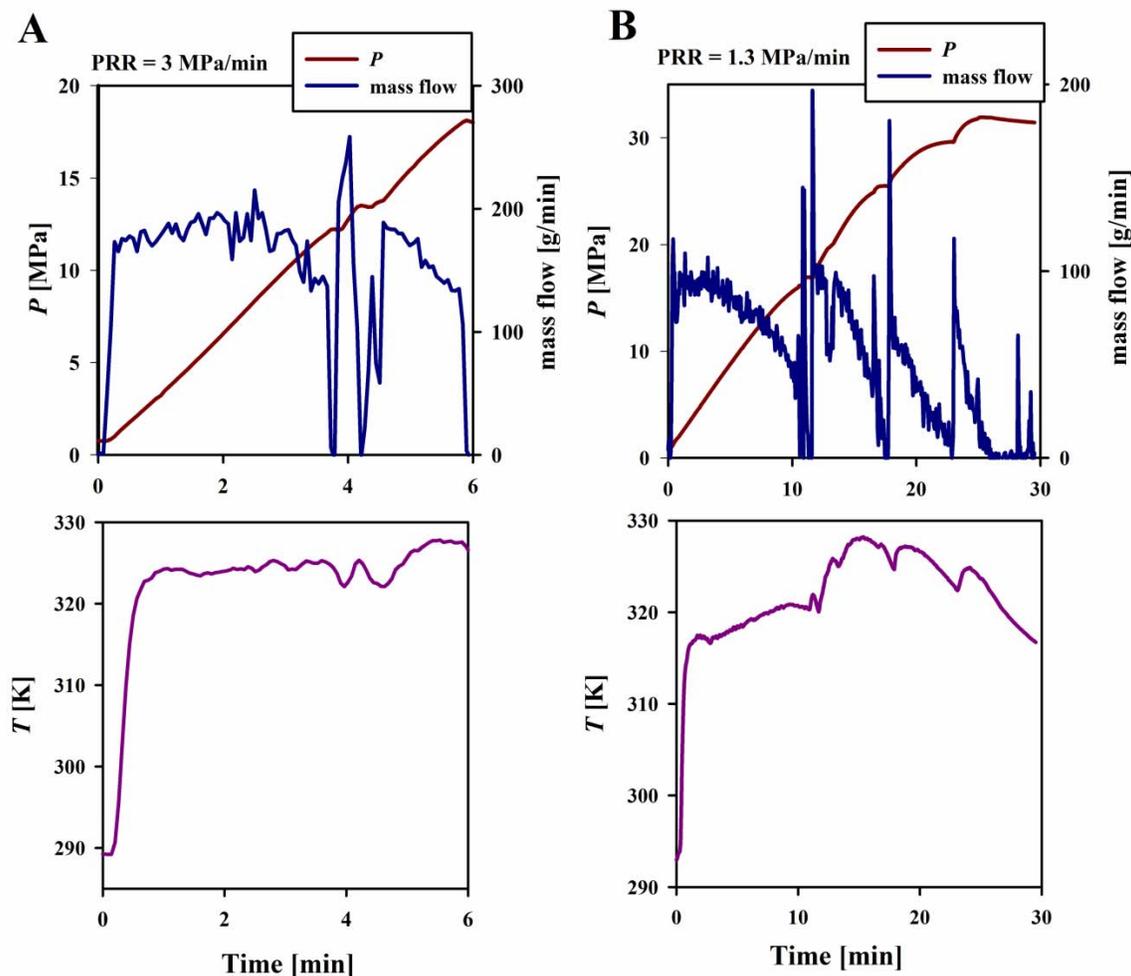


Fig. 5. Pressure, mass flow, and temperature for the FTS tank during the test draft of A) 1 kg and B) 1.6 kg He. In (A), at approximately 4 min, one high P tank was depleted and a second one opened to finish the collection. In (B), all four of the TFF high P tanks were used for the collection. At approximately 10 min, 18 min, and 24 min a high P tank was closed and another opened.

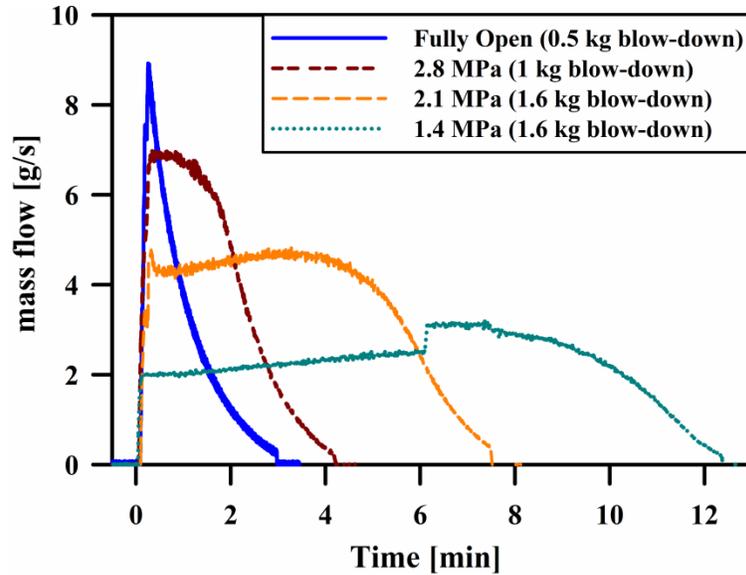


Fig. 6. Flow profiles of He gas being blown-down through the coriolis master meter.

4. Description of the Three Mass Measurement Methods

4.1 PVT method:

The mass dispensed (Δm_{PVT}) into the FTS is calculated by:

$$\Delta m_{PVT} = \rho_2 V_2 - \rho_1 V_1 ; \quad (1)$$

where ρ_1 and ρ_2 are the initial and final gas densities, and V_1 and V_2 are the initial and final volume of the FTS tank, respectively. The gas density is given by:

$$\rho = \frac{PM}{zRT} ; \quad (2)$$

where P is the gas pressure, M is the gas molar mass, R is the universal gas constant, T is the gas temperature, and z is the compressibility factor. The NIST properties database REFPROP [9] is used for density calculations. The FTS tank volume is a function of T and P and is given by:

$$V = V_{\text{ref}}[1 + \lambda\Delta P][1 + 3\alpha\Delta T] ; \quad (3)$$

where V_{ref} is the FTS tank volume at 20 °C and 101 kPa, $\lambda = 2.4 \times 10^{-7} \text{ kPa}^{-1}$ is the pressure expansion coefficient, $\alpha = 3.0 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ is the linear thermal expansion coefficient, and ΔT and ΔP are the difference of the temperature and pressure from the reference values, respectively. The thermal expansion coefficient was given by the manufacturer. The pressure expansion coefficient was calculated from manufacturer's values of the tank volume at 100 kPa and at 43 MPa. An expanded uncertainty of 20 % was assigned to each of these values because we are relying on manufacturer's data. Inserting Eqns. 2 and 3 into Eqn. 1 gives the governing equation for the mass dispensed via the PVT method:

$$\Delta m_{PVT} = \frac{V_{\text{ref}}M}{R} \left[\frac{P_2}{z_2 T_2} [1 + \lambda\Delta P_2][1 + 3\alpha\Delta T_2] - \frac{P_1}{z_1 T_1} [1 + \lambda\Delta P_1][1 + 3\alpha\Delta T_1] \right]. \quad (4)$$

4.1.1 Tank volume determination: We used the volume expansion method [10] to measure the volume $V_{\text{ref}} = 39,530 \text{ cm}^3$ at a pressure of 101 kPa with expanded uncertainty of 0.17 %.

4.1.2 Pressure measurements: For the laboratory tests, a resonant silicon gauge pressure transducer calibrated by the NIST Thermodynamic Metrology Group and two intrinsically safe analog sensors were used for pressure measurements. The resonant silicon gauge sensor has a higher accuracy than the analog sensors that use piezoelectric technology for sensing and is therefore called the 0.01 % pressure sensor. The analog pressure sensors were calibrated against the 0.01 % pressure sensor. The two analog sensors have ranges of 35 MPa (5000 psi) and 1.4 MPa (200 psi). The higher ranged sensor is used for measurements when the FTS tank is “full” and the lower ranged sensor is used when the FTS tank is “empty”. The 0.01 % pressure sensor is not intrinsically safe and therefore cannot be used for future field tests with H_2 . However, we compare measurements made with the analog sensors to those made with the 0.01 % pressure sensor during an 88-day interval. Over this interval, the higher-ranged pressure sensor agreed with the 0.01 % pressure sensor within 1.34 % when tank pressures were below 17 MPa (2500 psi) and within 0.65 % when pressures were above 17 MPa. The 1.4 MPa pressure sensor agreed with the 0.01 % pressure sensor within 0.65 % over its operating range. Therefore, the uncertainty in pressure measurements depends on the amount of gas dispensed into the FTS tank and whether the 0.01 % pressure sensor or the analog pressure sensors are used. The agreement of the analog sensors with the 0.01 % pressure sensor is taken as the upper limit of a rectangular distribution. Therefore the standard uncertainty in the pressure measurement made with the analog sensors ranges from 0.1 % to 0.77 %.

4.1.3 Temperature measurements: Four Inconel sheathed, ungrounded type K TCs were purchased for use in the FTS; two are spare and two were inserted into each end of the FTS tank (Fig. 2) and used for temperature measurements during the laboratory tests. A National Instruments¹ TC DAQ card was used to acquire the TC measurements. Before the two sensors were installed in the FTS, all four were calibrated against the Fluid Metrology Group’s reference temperature standards. The FTS will be used outdoors under a wide range of temperature conditions; therefore, an assessment of the cold junction compensation by the TC DAQ card was made.

The TCs were kept in a temperature controlled water bath with the reference sensors. First, the effect of a cold environment was tested. The DAQ box shown in Fig. 3 was placed outdoors in January where the temperature was 7.5 °C (45 °F). A thermistor placed inside the DAQ box measured a temperature of 9 °C after being outside for more than 3 hours. Of the four TCs, the maximum deviation from the reference was 0.14 °C and the minimum deviation was 0.001 °C. Second, the effect of a hot environment was tested. A heater was placed above the DAQ box with thermistors outside and inside of the box. The outside of the box reached 34 °C (93 °F) and the inside reached 31 °C. Of the four TCs, the maximum deviation from the reference was 0.32 °C and the minimum deviation was 0.16 °C. The results of the cold junction compensation tests show an extra uncertainty up of 0.32 °C may be introduced in the field tests. We assume that this uncertainty has a rectangular distribution.

To test the TC calibration drift over time, the two spare sensors were placed in a 1 L, insulated borosilicate beaker with two reference sensors. The two TCs were periodically compared to the reference sensors to observe the TC calibration drift. Ninety-six days after their calibration, the sensors drifted by a maximum of 0.20 °C ($\approx 0.09 \%$) (Fig. 7). This value is much greater than the calibration uncertainty. Therefore, for the laboratory tests, an uncertainty of 0.20 °C is used (with a rectangular distribution). The standard uncertainty in the temperature measurements ranges from $(0.32 + 0.2)/\sqrt{3} = 0.3 \text{ K}$ to $0.2/\sqrt{3} = 0.12 \text{ K}$ for field and laboratory tests, respectively.

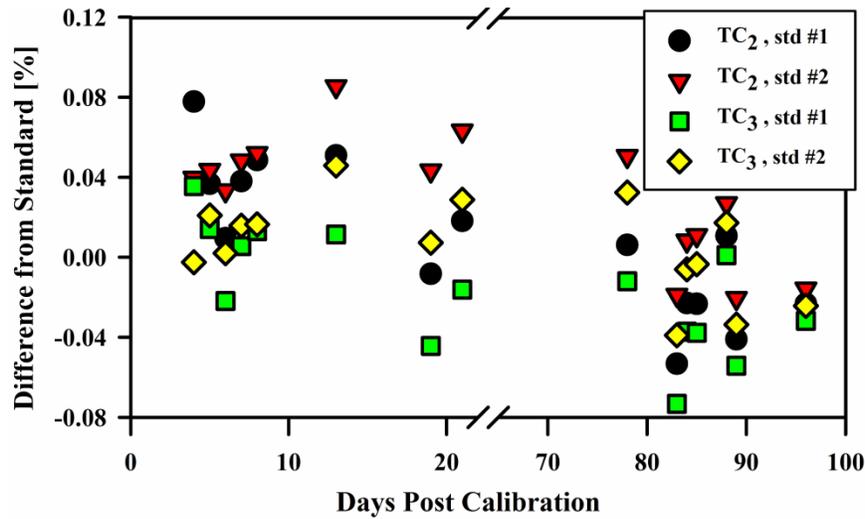


Fig. 7. Drift of TC calibrations used in the H₂ FTS over 96 days.

4.1.4 Expanded uncertainty in the PVT method measurement: The expanded uncertainty in the PVT measurement with coverage factor k can be calculated by:

$$\left[\frac{U(\Delta m_{PVT})}{k\Delta m_{PVT}} \right]^2 = \sum_{i=1}^9 S_{x_i}^2 \left(\frac{u(x_i)}{x_i} \right)^2 ; \quad (5)$$

where the x_i are the 9 measurands in Eqn. 4: V_{ref} , P_1 , P_2 , T_1 , T_2 , z_1 , z_2 , α , and λ and where S_{x_i} is the normalized sensitivity coefficient for each variable. The values of S_{x_i} are calculated by:

$$S_{x_i} = \frac{\partial \Delta m_{PVT}}{\partial x_i} \frac{x_i}{\Delta m_{PVT}} ; \quad (6)$$

Table 3 gives the uncertainty budget for the PVT method for a 0.5 kg test draft in the laboratory setting: 0.21 % ($k = 2$). In the laboratory, the largest contributors to the uncertainty are 1) the volume of the FTS tank followed by 2) the compressibility factor z_2 and 3) the final gas temperature. However, in the field we will use the larger uncertainty intrinsically safe pressure sensor and pressure becomes the dominating uncertainty component with the final tank pressure contributing as much as 96.5 % to the overall uncertainty.

Table 3. Uncertainty budget for the *PVT* method in the laboratory setting. Analysis is for 0.5 kg He gas collected.

Δm via <i>PVT</i>	Nominal Values	S_{xi} []	u_i [%]	$u_i^2 \cdot S_{xi}^2$	% contribution
V_{ref} [cm ³]	39530	1	0.083	6.9×10^{-3}	65.7
Tank <i>P</i> initial [kPa]	841	1.1×10^{-1}	0.01	3.7×10^{-7}	<0.1
Tank <i>P</i> final [kPa]	8963	1.11	0.01	4.0×10^{-5}	0.38
Tank <i>T</i> initial [K]	295	1.04×10^{-1}	0.04	1.6×10^{-4}	0.16
Tank <i>T</i> final [K]	296	-1.10	0.04	1.9×10^{-3}	17.7
Coefficient of linear expansion (α) [1/K]	3.0×10^{-6}	2.7×10^{-5}	10	7.1×10^{-8}	<0.1
Pressure expansion coefficient (λ) [1/kPa]	2.4×10^{-7}	2.4×10^{-3}	10	5.7×10^{-4}	5.5
Compressibility factor z_1	1.00	0.11	0.03	1.1×10^{-5}	0.1
Compressibility factor z_2	1.04	-1.11	0.03	1.1×10^{-3}	10.5
u_c [%]				0.11	
U_e ($k=2$) [%]				0.21	

4.1.5 Feasibility of the *PVT* method in field tests: There are two reasons why the *PVT* method is not ideal for field tests. First, the commercially-available, intrinsically-safe pressure sensors have significant calibration drift, making their measurements too unreliable for the 0.5 % uncertainty goal for the mass measurement. The highest ranged pressure sensor (35 MPa or 5000 psi) is the largest contributor to the uncertainty in the mass determined by the *PVT* method. As mentioned in section 4.1.2, the largest observed deviation in the readings from the 35 MPa range analog sensor and the 0.01 % pressure sensor at approximate pressure of 17 MPa (1 kg He) was 1.34 %. The manufacturer's specified uncertainty is 0.21 % at this pressure. The comparisons between this analog sensor and the 0.01 % pressure sensor made over eighty-eight days showed a shift of -21.5 kPa in the calibration gain and -124.1 kPa in the calibration zero. This calibration shift leads to an overall uncertainty in the mass measurement of 1.8 %. Therefore, the sensors we purchased for the field are not accurate enough to meet the 0.5 % measurement uncertainty goal.

The second disadvantage, shared with the master meter method, is that thermal equilibrium must be reached in the FTS before accurate T and P measurements can be made. Because field tests are repeated a minimum of three times at the MMQ and at the maximum capacity of the FTS tank [7], there are two times (for each test draft) when thermal equilibrium is necessary: 1) following the release of the previous test draft, and 2) following the fill of the current test draft. Figure 8 illustrates the process for three test drafts. This process is repeated a second time for the other quantity of gas to be collected. The time to wait depends on the atmospheric temperature and the temperature of the gas inside the FTS during a fill or blow-down. The wait time will increase as the temperature difference between the gas inside the tank and the atmosphere increases. The factors that influence this difference are 1) the rate of the fill (or PRR), 2) the volume of gas dispensed into the FTS, 3) the blow-down rate, and 4) the atmospheric conditions.

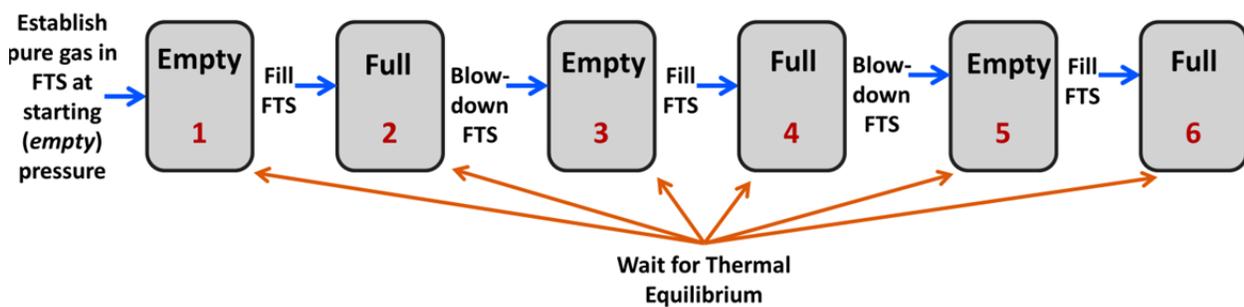


Fig. 8. Illustration of the number of times thermal equilibrium must be reached for the *PVT* method in the FTS during three repeats of the collection of a specified amount of gas.

To estimate the error introduced into the mass measurement by not waiting for thermal equilibrium when filling the FTS tank, the ratio of the density measured in the FTS tank once equilibrium is reached to that measured within 4 seconds of completing a fill was calculated. Figure 9 shows the density ratios for fills with 0.5 kg, 1 kg, and 1.7 kg He as a function of the temperature gradient between the gas inside the FTS tank and the room and as a function of the PRR. The PRR affects the temperature gradient between the inside of the FTS tank and the environment because the tank heats up due to gas compression while being filled. In general, the less mass dispensed into the tank and the lower the PRR, the less time until thermal equilibrium is reached.

Figure 10 shows the percent difference in the calculated gas mass if T and P measurements are made at one minute intervals following the emptying of the tank (from the prior test draft) and subsequently following the fill of the tank with 1 kg He. Initially, the mass measurement error is equivalent to that shown in Fig. 9. However, after waiting three minutes, the error diminishes from, in this case, 0.6 % to 0.15 %. After one hour, the error is less than 0.002 %.

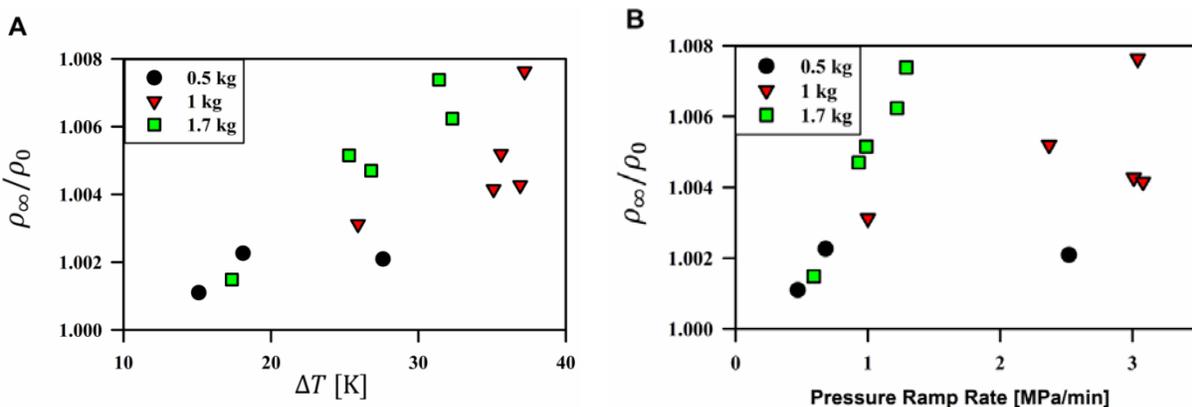


Fig. 9. A) Ratio of the density measured in the FTS tank once thermal equilibrium is reached to that measured within 4 seconds of completing a fill. ΔT is the difference between the temperature of the gas in the FTS and the room temperature. B) Density ratio as function of the PRR.

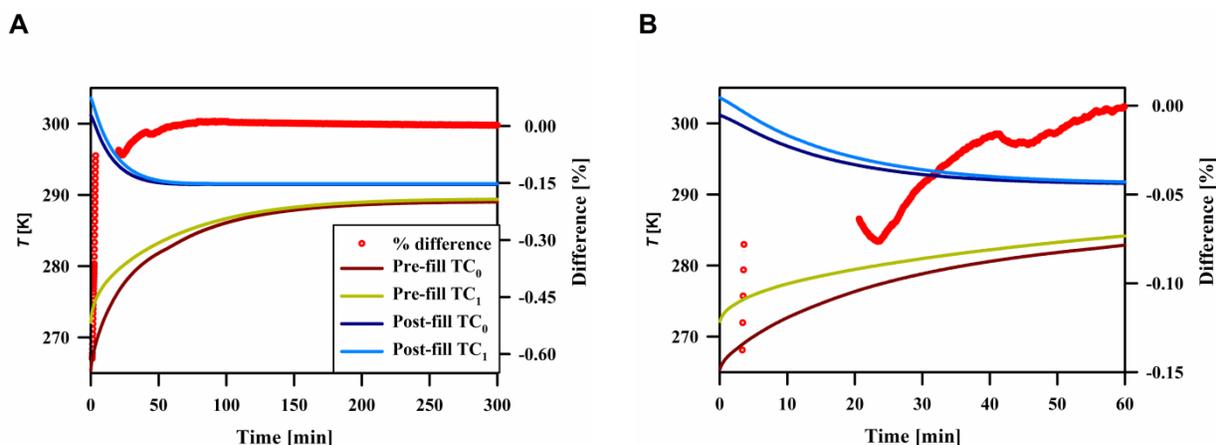


Fig. 10. Effect of not waiting for thermal equilibrium for the gas mass measurement via the *PVT* method. A) Difference in measured mass (at 1 min intervals) from mass measured at equilibrium and T profiles following gas release (pre-fill conditions) and for the subsequent fill with 1 kg He (post-fill conditions). B) Expanded time scale shows 20 min following a fill, the error in measured mass is less than 0.1 %. *Note:* In this case, the tank was weighed following the fill before the final *PVT* measurement and thus approximately 20 min of P and T data is absent.

4.2 Gravimetric Method:

The mass dispensed (Δm_{grv}) into the FTS is calculated by:

$$\Delta m_{\text{grv}} = m_2 - m_1, \quad (7)$$

where m is the true mass and the subscripts 1 and 2 denote the mass of the FTS pre-filling and post-filling, respectively.

The scale indicated mass (m_a) is buoyancy corrected to determine the true mass via the equation: $m = m_a + \rho_{\text{air}}V$; where ρ_{air} is the density of the air surrounding the tank, a function of atmospheric P , T , RH and the molar mass of air. V is the volume of the FTS tank. Therefore:

$$\Delta m_{\text{grv}} = m_{a2} + \rho_{\text{air}2}V_2 - [m_{a1} + \rho_{\text{air}1}V_1]. \quad (8)$$

The volume of the FTS tank is given by Eqn. 3. Inserting Eqn. 3 for the volume leads to the governing equation for mass determination for the gravimetric method:

$$\Delta m_{\text{grv}} = m_{a2} - m_{a1} + V_{\text{ref}}[\rho_{\text{air}2}[1 + \lambda\Delta P_2][1 + 3\alpha\Delta T_2] - \rho_{\text{air}1}[1 + \lambda\Delta P_1][1 + 3\alpha\Delta T_1]]. \quad (9)$$

4.2.1 Uncertainty in the gravimetric measurement method: The uncertainty in the gravimetric measurement can be calculated by:

$$\left[\frac{U(\Delta m_{\text{grv}})}{k\Delta m_{\text{grv}}} \right]^2 = \sum_{i=1}^{11} S_{x_i}^2 \left(\frac{u(x_i)}{x_i} \right)^2, \quad (10)$$

where the x_i are the 11 measurands in Eqn. 9: m_{a1} , m_{a2} , V_{ref} , P_1 , P_2 , T_1 , T_2 , $\rho_{\text{air}1}$, $\rho_{\text{air}2}$, α , and λ and where S_{x_i} is the normalized sensitivity coefficient for each variable. The values of S_{x_i} are calculated with Eqn. 6 by replacing Δm_{PVT} with Δm_{grv} .

The weigh scale used in these measurements has resolution of 1 g and that is the largest contributor to the uncertainty in the gravimetric measurement. Calibration of the scale against NIST standard masses introduces a gain correction factor of 0.02 % from unity. An atmospheric monitor was used to measure the air density with uncertainty of 0.32 % ($k = 1$). Because the temperature and pressure measurements inside the FTS tank that were discussed in detail in Section 4.1 are only used for determining the FTS tank volume for buoyancy corrections, their combined contribution to the overall uncertainty budget is $< 10^{-4}$ %. Table 4 gives the uncertainty in the gravimetric measurement for a test draft of 0.5 kg helium (0.57 %). For 1 kg measurements, the uncertainty is half of that for 0.5 kg measurements.

4.2.2 Importance of buoyancy corrections: The conventional correction factor for buoyancy effects used by scale manufacturers to turn apparent mass readings into true mass readings is $1 - \rho_{\text{air}}/\rho_{\text{steel}}$, where the conventional values for the density of air and steel are 1.2 kg/m^3 and 8000 kg/m^3 , respectively at $P = 101.325 \text{ kPa}$, relative humidity (RH) = 50 %, and $T = 293.15 \text{ K}$. The density of steel is used because the masses used to calibrate scales are made of steel. If the air density is not this conventional value, additional buoyancy corrections must be made for measurements of the lowest uncertainty.

In the laboratory tests, room T , P , and RH measurements were made simultaneously with the gravimetric measurements in order to make buoyancy corrections. Changes in room T , RH , and P between the weighing of the “empty” and the “full” FTS of 1.5 K, -2.6 %, and -300 Pa were observed. If buoyancy corrections were ignored during our 0.5 kg laboratory tests, mass measurement errors as large as 0.038 % would result.

To estimate the maximum importance of making buoyancy corrections in the field, we considered extreme environmental conditions. The day time T , RH , and barometric P during the winter and summer seasons were investigated for multiple locations within the United States. Of the locations we considered, the location with the highest day time air density is Anchorage, Alaska in the winter. The location with the lowest day time air density is Alma, Colorado in the summer. Alma, Colorado is approximately 3 km above sea level; therefore, Phoenix Arizona was also investigated and found to have the next lowest day time air density in the summer. Table 5 gives the parameters for these locations. Figure 11 shows the error in the gravimetric measurement if buoyancy corrections are not made in these locations. The error has been

calculated for the non-conventional atmospheric conditions with 1) no change in conditions between weighing the “empty” and “full” FTS and 2) assumed changes in T , RH and barometric P of 5 K, 3 %, and 300 Pa. These changes are reasonable estimates of what will be encountered during field tests and therefore give an estimate of the error in gravimetric measurements if they are not buoyancy corrected. These corrections become more significant as the atmospheric density increases from the conventional value, as in Anchorage AK, where the error is as large as 0.12 % with the mentioned changes in atmospheric conditions.

Table 4. Uncertainty budget for the gravimetric method in the laboratory setting. Analysis is for 0.5 kg He gas collected.

Δm via Gravimetric Method	Nominal Values	S_{xi} []	u_i [%]	$u_i^2 * S_{xi}^2$	% contribution
m_a initial [kg]	79.7	-159.4	1.2×10^{-3}	4.0×10^{-2}	48.9
m_a final [kg]	80.2	160.4	1.3×10^{-3}	4.0×10^{-2}	48.9
ρ_{air} initial [kg/cm ³]	1.2×10^{-6}	0.09	0.31	8.9×10^{-4}	1.1
ρ_{air} final [kg/cm ³]	1.2×10^{-6}	-0.09	0.31	8.9×10^{-4}	1.1
V_{ref} [cm ³]	39530	1.8×10^{-4}	0.084	2.2×10^{-10}	<0.1
Tank P initial [kPa]	160	-3.7×10^{-6}	0.01	4.3×10^{-16}	<0.1
Tank P final [kPa]	8160	1.9×10^{-4}	0.01	1.1×10^{-12}	<0.1
Tank T initial [K]	303	-1.0×10^{-8}	0.04	1.5×10^{-19}	<0.1
Tank T final [K]	293	5.0×10^{-7}	0.04	3.8×10^{-16}	<0.1
Coefficient of linear expansion (α) [1/K]	3.0×10^{-6}	-8.6×10^{-9}	10	7.5×10^{-15}	<0.1
Pressure coefficient (λ) [1/kPa]	2.4×10^{-7}	-8.6×10^{-9}	10	7.5×10^{-15}	<0.1
u_c [%]				0.29	
U_e ($k=2$) [%]				0.57	

Table 5. Daytime atmospheric conditions at several United States locations and the difference in air density from the conventional value of 1.2 kg/m^3 .

Location	Air T [K]	Barometric P [kPa]	RH [%]	ρ_{air} [kg/m^3]	Difference from conventional value [%]
Phoenix, AZ (summer)	314	100	20	1.104	-7.97
Anchorage, AK (winter)	267	98.4	73	1.283	6.89
Alma, CO (summer)	297	64	21	0.748	-37.66
Gaithersburg, MD (winter)	295	99.1	41	1.168	-2.69

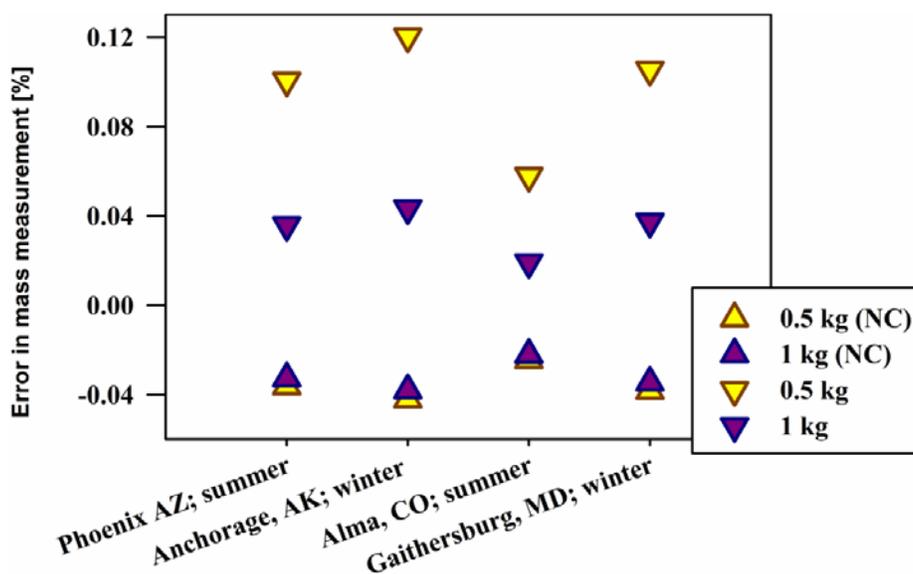


Fig.11. The symbols show the error in mass measurements of 1 kg and 0.5 kg at 4 locations in the United States. The upward arrows represent error for non-conventional atmospheric conditions with no change in conditions between weighing the “empty” and the “full” FTS. The downward arrows represent the error if the non-conventional conditions change by 5 K, 3 % RH and 300 Pa.

4.3 Master meter method:

Following the fill of the FTS tank, the gas is blown-down through a coriolis master meter. The mass that filled the FTS tank (Δm_{MM}) is calculated by:

$$\Delta m_{MM} = \Delta m_{CM} + \Delta m_{FTS} + \Delta m_{CV} , \quad (11)$$

where Δm_{CM} is the mass totalized by the coriolis master meter, Δm_{FTS} and Δm_{CV} are the change in mass in the FTS tank and in the connecting volume between the FTS tank and the coriolis master meter, respectively, before and after blow-down through the master meter (mass post

blow-down – mass pre-filling). The connecting volume is less than 9 cm³, less than 0.022 % of the FTS tank volume and therefore, mass measurements in it can be neglected without significant measurement uncertainty (Table 6).

4.3.1 Calibration of the master meter: The master meter is a coriolis meter with two 0.15 cm diameter flow tubes. The meter was calibrated under steady state conditions on NIST's *PVTt* system [11]. The master meter is used as received from the manufacturer in these tests and therefore corrections are not made to its readings. The meter agreed within 0.36 % under steady flow conditions. Figure 12(A) shows the results from this steady state calibration. The 0.36 % can be treated as the boundary value in a rectangular distribution so the meter has a base standard uncertainty of 0.21 %.

In experiments independent from those used to produce Fig. 1, we used the *PVT* system to assess the uncertainty in the master meter due to the transient conditions of the FTS (see Fig. 6). Figure 12(B) shows the agreement between the two methods for these experiments (< 0.19 %). The 0.19 % can be treated as the boundary value in a rectangular distribution so the meter has added standard uncertainty due to usage during transient flow of 0.11 %. The steady state uncertainty root-sum-squared with the transient uncertainty leads to an overall standard uncertainty for the totalized mass according to the master meter of 0.24 %.

4.3.2 Uncertainty in the master meter method: The uncertainty in the gravimetric measurement can be calculated by:

$$\left[\frac{U(\Delta m_{MM})}{k\Delta m_{MM}} \right]^2 = \sum_{i=1}^3 S_{x_i}^2 \left(\frac{u(x_i)}{x_i} \right)^2, \quad (12)$$

where the x_i are the 3 measurands in Eqn. 11: Δm_{CM} , Δm_{FTS} , and Δm_{CV} and where S_{x_i} is the normalized sensitivity coefficient for each variable. The values of S_{x_i} are calculated with Eqn. 6 by replacing Δm_{PVT} with Δm_{MM} .

Taking the partial derivative of Eqn. 11 for each component shows that the sensitivity coefficients are directly proportional to the fraction of total mass each component represents. The closer the mass in the FTS tank is following the blow-down through the master meter to that before the FTS tank was filled, the less Δm_{FTS} contributes to the overall uncertainty. The largest change in this mass during the laboratory tests was 18.7 g of He, which represents a 288 kPa (42 psi) change at constant temperature of 290 K. The uncertainty in this measurement in the laboratory setting (and therefore negligible uncertainty due to cold junction compensation and with the 0.01 % pressure sensor for pressure measurements) is less than 0.12 %. Using the analog pressure sensor with 0.37 % uncertainty ($k = 1$) and taking into consideration the added uncertainty in temperature measurements due to cold junction compensation errors increases this value to 0.17 %. Table 6 shows the uncertainty budget for the master meter measurement method for 0.5 kg He collection using the larger field uncertainty values for Δm_{FTS} .

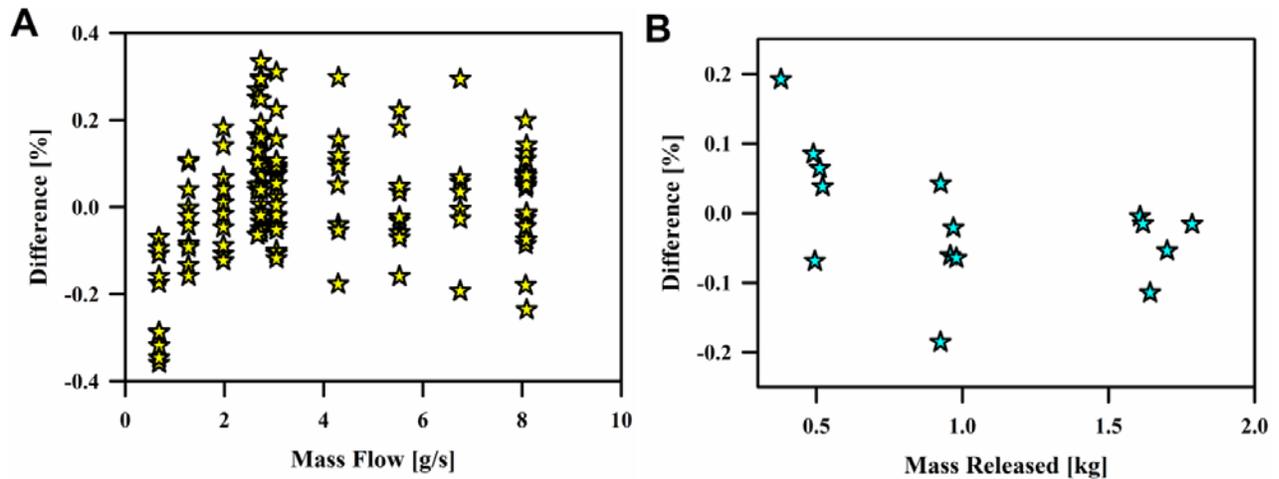


Fig. 12. A) Difference between the master meter and NIST's *PVTt* primary standard during steady flows. B) Difference between the master meter and *PVT* measurements made during the blow-down of the collected mass from the FTS tank during the laboratory tests.

4.3.3 Effect of measurement errors in Δm_{FTS} : Measurements will be repeated multiple times in the field tests. Therefore, gas will be blown-down from the FTS tank before it is filled for the next test multiple times. The consequence of this is the temperature of the gas left in the tank following the blow-down is initially cold, but will warm to the environmental temperature. Because the T and P sensors have response time lags, the density measurements made following the release of gas have errors from the un-steady conditions. In the field, it may be difficult to wait for thermal equilibrium. Therefore, it is necessary to estimate the contribution of unsteady conditions to the uncertainty of the master meter method.

Table 6. Uncertainty budget for the master meter method in the field setting. Analysis is for 0.5 kg He gas collected.

Δm via the master meter method [kg]	Nominal Values	S_{xi} []	u_i [%]	$u_i^2 \cdot S_{xi}^2$	% contribution
Δm_{CM} [kg]	0.50	.96	0.235	5.1×10^{-2}	99.9
Δm_{CV} [kg]	4.9×10^{-6}	9.4×10^{-6}	100	8.8×10^{-7}	<0.1
Δm_{FTS} [kg]	2.2×10^{-2}	4.3×10^{-2}	0.17	5.4×10^{-5}	0.11
u_c [%]				0.23	
$U_e (k=2)$ [%]				0.46	

Δm_{FTS} is zero if the mass in the FTS tank following the blow-down through the master meter is equal to the mass in the tank before filling, and hence, there is no need to make density measurements for the master meter measurement method. However, it is impractical to

achieve this condition. The measurement error added by not waiting for thermal equilibrium and not having $\Delta m_{\text{FTS}} = 0$ was quantified. The FTS was filled with 1 kg He. The He was blown-down from the FTS tank and measurements were made from the T and P sensors continuously following the blow-down (Fig. 13(A)). Readings from the sensors were averaged every minute while thermal equilibrium was reached and the mass calculated; this is the starting mass in the FTS for the master meter method. This data was used to simulate the conditions in the FTS following a fill and blow-down through the master meter, however, it was altered to not match the pre-fill conditions: T was increased by 5 K and the P by 173 kPa (25 psi), 345 kPa (50 psi), or 690 kPa (100 psi). Figure 13(A) illustrates the P and T profile for the 345 kPa increase case. The mass dispensed into the FTS tank (Δm_{MM}) was calculated using the average density measurements while the tank gas was not at thermal equilibrium and compared to the calculated Δm_{MM} value at equilibrium. Figure 13(B) shows the added measurement error as a function of wait time and as a function of not returning to the pre-fill tank pressure. To keep the measurement uncertainty below 0.5 %, the added uncertainty should not be larger than 0.04 %. This requires wait times of 20 minutes if the starting pressure is within 173 kPa of the ending pressure. This wait time increases to 1.5 hours if the pressure change is as large as 690 kPa. Therefore, for measurements that meet the desired uncertainty, the starting (or pre-fill) pressure should be kept within 173 kPa of the ending (or post blow-down) pressure. Planned field tests will better define what wait time should be used.

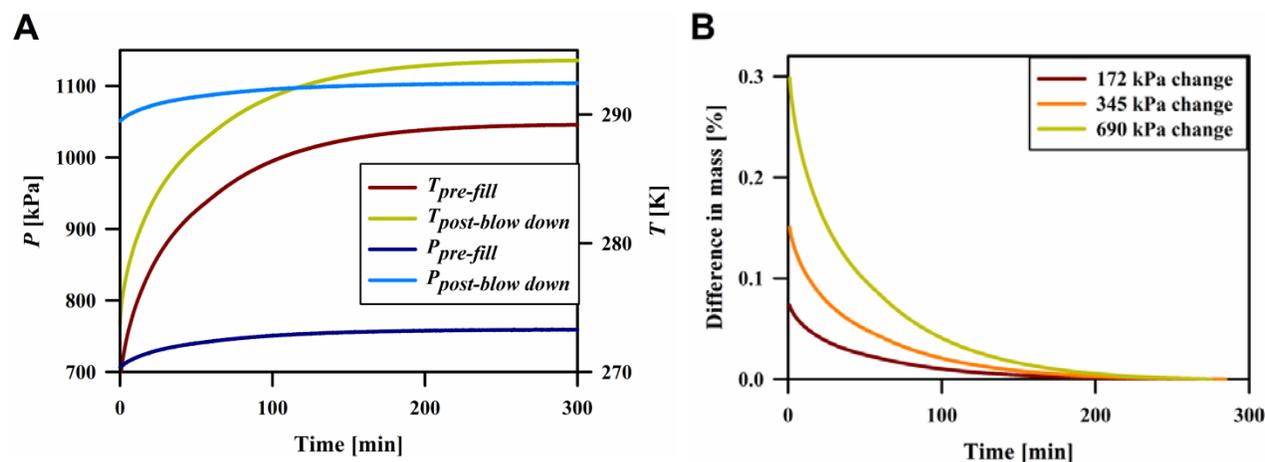


Fig. 13. A) P and T profile of the FTS tank gas following the blow-down of 1 kg helium gas. B) Added uncertainty in the master meter method measurement for not waiting for thermal equilibrium during Δm_{FTS} measurements.

5. Summary of Laboratory Tests

All three methods (PVT , gravimetric, and master meter) incorporated into the FTS agree within 0.57 %. All methods allow a gaseous dispenser to perform as it would while filling the compressed gas tank of a small vehicle. However, not all methods are equally practical in the field.

Table 7 summarizes each method's uncertainty, estimated hardware cost, and the time required to perform six test drafts. The time for 6 test drafts assumes it takes 30 minutes to fill the FTS with 1 kg He, 20 minutes to reach thermal equilibrium when needed, 10 minutes to weigh the FTS when needed, and 10 minutes to blow-down the FTS through the master meter. The estimated cost is strictly for the materials we purchased and used to construct the FTS

presented in this manuscript. It does not include the labor cost of constructing the FTS, calibration of equipment, and support of equipment such as pre-test and post-test calibration checks. The estimated cost was calculated as if each method was a standalone FTS. For example, the type 3 cylinder is needed for all three methods and hence its cost is included in each method's estimate. The gravimetric method does not need a DAQ system because the scale can be read directly, therefore, that cost is not included

Table 7. Comparison of three field standard methods.

Method	Lab uncertainty (0.5 kg collection) ($k = 2$, %)	Field uncertainty (0.5 kg collection) ($k = 2$, %)	Estimated Cost (\$)	Time for 6 test drafts (h)
<i>PVT</i>	0.21	1.8	18K	7.5
Gravimetric	0.57	0.57	26K	5.8
Master Meter	0.45	0.45	29K	6.3

The lowest uncertainty measurement is the *PVT* performed in the laboratory with a 0.01 % pressure sensor (resonant silicon gauge). However, we were unable to find commercially-available, high accuracy pressure sensors for use with H₂; therefore, the uncertainty in this method increased to as much as 1.8 % (Table 1). The H₂-compatible pressure sensors that we purchased drifted so much that the measurement uncertainty exceeded the 0.5 % target. As shown in Section 4.1.5, waiting for 20 minutes for thermal equilibrium is adequate for mass measurements with less than 0.5 % uncertainty if the pressure measurements are as accurate as in the laboratory setting. The waiting time depended on heat transfer from the FTS tank to the environment. If a tank with better heat transfer were available, less time would be needed for thermal equilibrium and the FTS could make faster measurements.

The gravimetric method takes the least amount of time, and if atmospheric conditions are close to the conventional conditions, buoyancy corrections account for < 0.04 % of the measurement uncertainty. The magnitude of the added measurement uncertainty will depend on: 1) the mass being weighed, 2) the deviation of the atmospheric density from the conventional value, and 3) the change in atmospheric conditions between weighing the “empty” and the “full” FTS. In the laboratory tests, the buoyancy correction was as large as 0.038 %. An environmental monitor can account for environmental changes between weighing the “empty” and “full” FTS (Section 4.2.2). Aside from buoyancy corrections, the scale with the capacity needed to weigh the FTS has only 1 g resolution making it the largest uncertainty contributor in this measurement and it is a costly piece of equipment.

The master meter method meets the measurement accuracy requirement of 0.5 %. If the change in mass in the FTS tank (Δm_{FTS}) is less than 2 % of Δm_{CM} , density measurements can be made within 20 minutes following the blow-down of the collected mass through the coriolis master meter. The master meter method has a significant disadvantage; the meter cannot be easily verified in the field. The meter used in these experiments was carefully handled and was tested extensively under transient flow conditions. The need for field verification could be circumvented by using two master meters in series. This allows the operator to check for consistent measurements and will flag calibration drift, but will raise the component cost of the FTS. If the two meters in series used different sensing technology, they are unlikely to be subjected to the same drift or sensitivity to temperature and vibration.

The tests described here indicate that all three methods can achieve 0.57 % or less uncertainty for a H₂ field test standard for 0.5 kg of gas. The uncertainty is < 0.57 % for larger masses of gas. The laboratory tests and uncertainty analyses give guidance on the importance of proper measurements for each method. We have also gained insight on the relative performance regarding completion time and ease of use of the three methods.

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