A Comparison of Primary Gas Flow Standards Spanning the Range 10 sccm N_2 to 10 slm N_2

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Abstract:

We describe an international comparison of gas flow standards spanning the range 2.1 x 10^{-4} g/s (10 sccm) of nitrogen to 0.21 g/s (10 slm) of nitrogen. For all the participating laboratories, $|E_n| < 0.78$, where E_n is the difference between the participant's result and the comparison reference value divided by the uncertainty of this difference. The $k = 2$ uncertainties (corresponding to 95 % confidence level) of the comparison reference values range from 0.036 % to 0.052 %. These comparison uncertainties include a contribution of 0.042 % from the uncertainty of the three laminar flow elements used as transfer standards. The participating laboratories were: Laboratoire National de Métrologie et d'Essais (LNE), National Institute of Standards and Technology (NIST), Fluke Primary Pressure and Flow Laboratory, Phoenix Arizona USA (FCP), Český Metrologický Institut (CMI), and Physikalisch-Technische Bundesanstalt (PTB).

1 Introduction

In June 2011, Laboratoire National de Métrologie et d'Essais (LNE) acquired a new primary gravimetric flow standard (GFS). Then, LNE needed to accredit this new standard with the Comité Français d'Accréditation (COFRAC). Any qualification or accreditation of a new standard requires understanding exactly how the standard operates and the uncertainties involved. LNE recognized that the understanding can be gained efficiently by participating in a comparison with other standards and laboratories. Thus, LNE's need for accreditation motivated this comparison.

This comparison was not intended to strictly follow the available guidelines for comparisons, e.g. ISO 17043 “Conformity assessment -- General requirements for proficiency testing” or NCSLI RP-15 “Interlaboratory Comparisons”. Instead, this comparison is an informal one, even though all of the participants have experience with inter-laboratory comparisons and proficiency testing, not all of the requirements from documentary standards were used, for example the participants shared their results during the comparison.

Fluke Calibration provided the transfer standard artifacts and related equipment and performed the initial calibration of the transfer standards. Seeking the involvement of another national lab, LNE obtained the cooperation of Dr. Wright at NIST and four flow references at NIST. When he learned of NIST’s participation, Dr. Kramer at PTB immediately expressed interest in participating. Encouraged by the level of interest and the fact that the artifacts would already be in the European Union, Fluke Calibration then invited Dr. Krajicek at CMI to participate and he accepted.

The comparison measurements were conducted from early 2011 until late 2012 and then the artifacts were returned to Fluke Calibration. During preparation of this paper, Fluke Calibration recalibrated the artifacts in January 2014 to “close the loop”. The calibration stability of the transfer standards during the comparison was assessed via the repeated calibrations at FCP and at LNE (as described in a later section of this paper) and included in the comparison uncertainty calculations.

For ease of reading, the mass flow units from this point forward will be stated in the equivalent standardized volumetric flow units of sccm[1]:

A mass flow of 2.1 x 10^{-4} g/s N_2 is stated as 10 sccm
A mass flow of 2.1 x 10^{-3} g/s N_2 is stated as 100 sccm
A mass flow of 2.1 x 10^{-2} g/s N_2 is stated as 1000 sccm
A mass flow of 2.1 x 10^{-1} g/s N_2 is stated as 10 000 sccm

Unless otherwise stated, all uncertainties in this document have coverage factor $k = 2$ corresponding to an approximately 95 % confidence interval.

2 Transfer Standards

The transfer standards were three molbloc[2] laminar flow elements with full scale flows in N_2 of:

100 sccm for serial number 3436
1000 sccm for serial number 3372
10 000 sccm for serial number 3410

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[1] Standard volumetric flow reference conditions are 101.325 kPa and 0° C.

[2] Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by NIST, LNE, PTB, or CMI, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Instrumentation for pressure and temperature measurement and flow calculation of the transfer standard elements (a molbox[2]) #787 was shipped as part of the transfer standard to reduce uncertainties that would be introduced by using different instrumentation in each lab. Each molbloc was used at 10 %, 25 %, 50 %, 75 %, and 100 % of its full scale flow and therefore this comparison covered three decades of flow from 10 sccm to 10 000 sccm. The transfer standard elements were calibrated in the downstream position where the outlet of the molbloc is intended to vent to an atmospheric pressure between 85 kPa and 105 kPa absolute. The downstream position also increases the differential pressure across the molbloc by 60 %, which assists in efforts to keep the uncertainties low.

3 Fluke Calibration – Phoenix USA Calibrations

The transfer standards were initially adjusted and calibrated using a dynamic gravimetric flow standard (dGFS) as shown in Figure 1, at Fluke Calibration – Phoenix, USA (FCP) in May and June of 2011. Note that the artifact shown in Figure 1 is representative only; it is neither the standard used for the comparison nor is it installed in the downstream position.

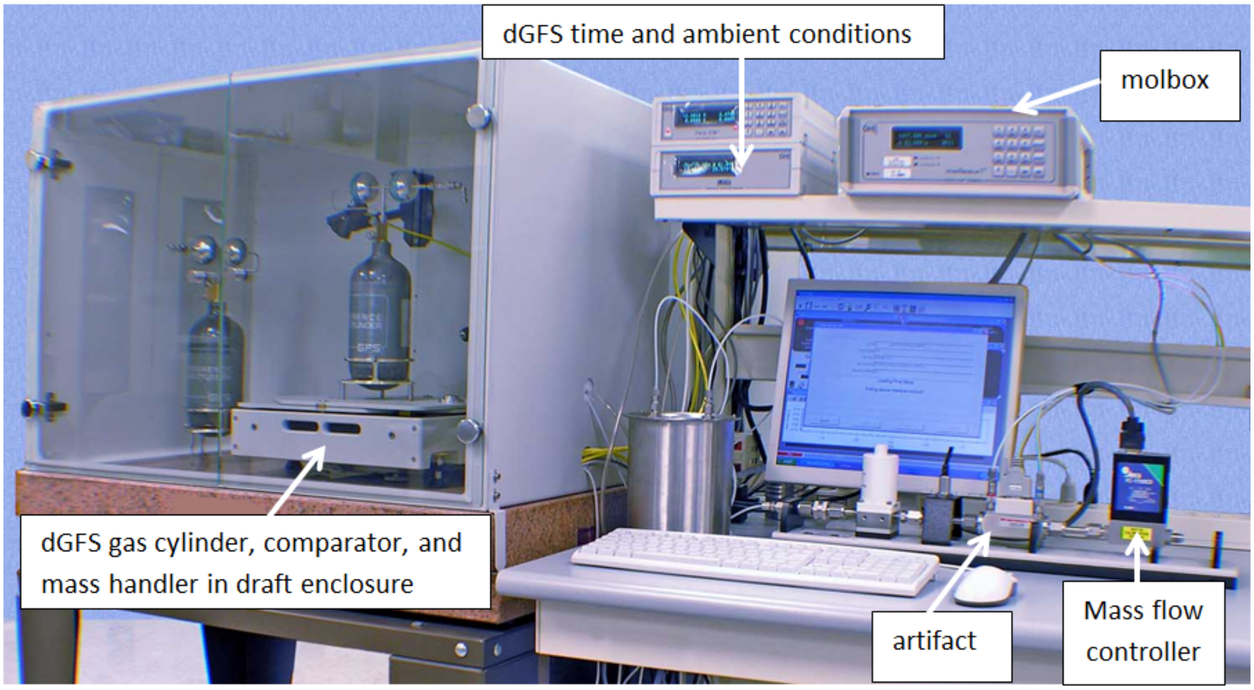


Figure 1: dGFS Gravimetric Flow Standard at FCP.

The dGFS [1] periodically measures the mass of a gas-filled, high-pressure cylinder while gas is withdrawn from the cylinder over a period of time (typically minutes to hours). The changes of the filled cylinder's mass are independent of the thermodynamic conditions and of the chemical composition of the gas in the cylinder. Thus, the cylinder's mass changes provide the mass flow from the fundamental SI units of mass (m) and time (t):

$$\dot{m} = \frac{dm}{dt} \cong \frac{m_{i+1} - m_i}{t_{i+1} - t_i} \quad , \tag{1}$$

where the subscripts i and i+1 represent successive time steps.

The dGFS consists of an electronic mass comparator, draft enclosure, automated mass handler, gas cylinder(s), flow controls, equipment for measuring time and ambient conditions, and a computer with specialized software that operates the system. These components provide automated data collection and recording, including the calibrated mass, time, pressure, temperature, and humidity measurements required to make accurate real-time mass flow measurements with continuous compensation for buoyancy corrections to the apparent weight of the cylinder.

Some advantages of a dynamic gravimetric over a static gravimetric system are that a static system requires the test cylinder to be disconnected and weighed before the start of a flow test and again at the end of the test, with associated uncertainties for the start and stop flow ramps, and data is only available after the final weighing.

The dynamic gravimetric system records independent time-stamped readings of the mass comparator at a typical rate of 5 times per second and associated instruments once per second. The test cylinder is an aluminum cylinder with a carbon fiber and epoxy overwrap to reduce mass while maintaining a 20 MPa pressure rating, with a specialized dual regulator assembly for a stable output pressure, available in a 1.1 liter size with a mass of ~1630 grams empty and 700 kPa outlet pressure, or a 1.5 liter size with a mass of ~2050 grams empty and 550 kPa outlet pressure. The test cylinder is supported by the mass comparator and it is always connected to the flow path. To minimize and stabilize unaccounted forces on the comparator, the flow path connection is a flexible 1.6 mm (0.0625 in) PFA polymer tube with an inside diameter of 0.76 mm (0.03 in) and a 1.4 MPa pressure rating, hanging in the form of a catenary loop between the cylinder and the downstream parts of the flow path. The ends of the catenary loop are miniature quick connects to allow disconnecting the test cylinder for filling or changing gases. The catenary loop is approximately 35 grams total mass, but due to the catenary shape and connection points results in a net added mass measured by the mass comparator of approximately 17.5 grams when connected to the test cylinder. Within the current *mass flow* range of the dGFS, gas diffusion through the PFA catenary has been considered to be insignificant based upon data collected in a variety of gases versus expected results, but alternate materials and methods are being considered and tested as research to lower the minimum flow capability continues. The flexible catenary connection also allows the system to use the automated mass handler to check and compensate for drift of the mass comparator over time. Each check exchanges the gas cylinder with a standard mass, weighs the standard, and returns the cylinder to the comparator. These checks do not alter the flow or stop the test. The stable catenary loop in the flow path allows the flow to be established and stabilized prior to the start of a test collection.

The typical reference standard expanded ($k = 2$) uncertainties during the course of the measurements taken by FCP for this comparison ranged from 0.09 % to 0.05 % of reading. For simplicity and conformity of the reported uncertainty for this paper, FCP chose to use the lab ISO17025 accredited expanded uncertainty of 0.10 % of reading as the expanded uncertainty of the dGFS for all individual test points. We note that the dGFS can achieve lower uncertainties, depending on the flow and amount of test gas depleted [2].

After FCP finished the calibration of the transfer standards, the standards and associated hardware were packaged and shipped to NIST in Gaithersburg, Maryland.

4 NIST Calibrations

During mid-to-late June of 2011, NIST used four flow references to calibrate the transfer standards: 1) the 34 L *PVTt* standard, 2) the 34 L tank using the Rate of Rise (RoR) method, 3) a dynamic Gravimetric Flow Standard (dGFS), and 4) the Working Gas Flow Standard (WGFS) using critical flow venturis.

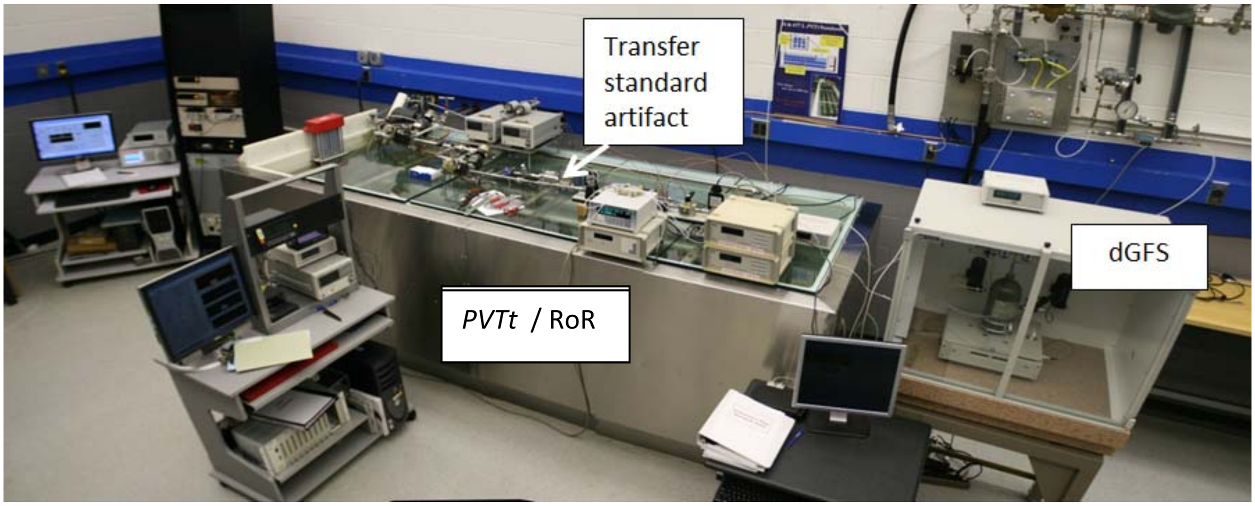


Figure 2: Three of the four flow references used at NIST.

4.1 NIST *PVTt*

NIST's 34 L Pressure-Volume-Temperature-time (*PVTt*) standard measures the change in the mass of gas within a well-known volume [U(volume) = 0.01 %] to provide a reference flow value. The *PVTt* mass flow is based on the change in the pressure and temperature in the collection tank between empty and full conditions. The NIST 34 L and 677 L *PVTt* standards have additional features that result in an uncertainty of 0.025 % or better [3]. Specifically, the collection tanks are in a temperature controlled water bath and the collection tanks have diameter of 200 mm or smaller for rapid thermal equilibration with the surrounding water. NIST's flow measurement protocol uses mass cancellation for the inventory volume, *i.e.* the stop time is chosen by the data acquisition and control program such that the pressure in the connecting volume between the device under test and diverting valves at the stop time matches the pressure at the start time. This leads to zero inventory volume corrections because of equal start and stop inventory masses (within uncertainty estimates) [4]. Generally, a 100 kPa inventory pressure is used, but the transfer standards were calibrated at a downstream pressure of 100 kPa and it is necessary to isolate a laminar flow meter from the pressure changes as the *PVTt* collection tank fills. Therefore, we used a back pressure regulator between the transfer standards and the *PVTt* diverter valves (see Figure 3) to provide a stable pressure (100 kPa ± 5 kPa) at the outlet of the transfer standards while the collection tank pressure increased from 0.02 kPa to 50 kPa ± 10 kPa during a collection. A mass flow controller established the desired flow set point and a pressure regulator provided stable pressure input of nitrogen to the mass flow controller. The *PVTt* results were used in the comparison for flows between 100 sccm and 2500 sccm.

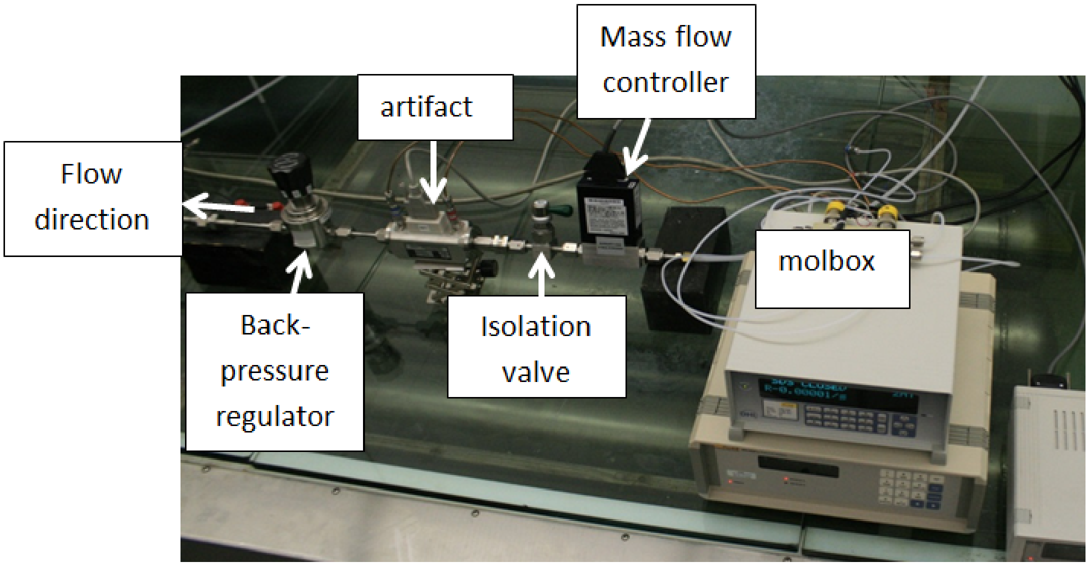


Figure 3: Test section for 10,000 sccm artifact on the 34 L *PVTt*.

4.2 NIST RoR

The Rate of Rise (RoR) method uses the same hardware and data acquisition software as the *PVTt*, but instead of determining the gas density in the collection tank at particular start and stop times, the RoR method records the pressure and temperature in the 34 L tank every 10 s. The recorded data is used to calculate the rate of change of mass $\dot{m}$ during the tank filling process. In the NIST RoR system, the volume is assumed constant and the temperature is assumed equal to the surrounding water bath. The mass flow is:

$$\dot{m} = \frac{d}{dt}[V\,\rho(P,T)] \cong V\left[\frac{\rho(P_{i+1},T_{i+1})-\rho(P_i,T_i)}{t_{i+1}-t_i}\right], \qquad (2)$$

where the subscripts i and i+1 represent values from sequential 10 s time increments and $\rho(P,T)$ is calculated from the NIST properties database REFPROP [5].

RoR measurements are a time-saving way to use a collection tank to calibrate small flows: a 10 sccm flow would take more than 2 days to fill the 34 L tank to 100 kPa, but a RoR measurement will take as little as 1 h. In practice, noise from pressure measurements leads to noise in RoR data. To illustrate the problem, at the lowest flows, pressure transducer readings fluctuate by the transducer's resolution. Occasionally, these fluctuations will result in incorrect negative values when the flow is calculated using Eq. (2). A boxcar filter was used, with flow set point stabilization times of greater than 5 h, and averaging times of greater than 30 min for these tests. The averaging periods were selected so that only stable RoR and meter under test data were used. The standard deviation of the mean of five or more sequential averages was used to assess repeatability. It is important to note that the collection volume for a RoR calibration does not equal the collection volume for the *PVTt* calibration because it also includes the connecting volume between the diverter valves and the exit of the device under test (DUT). The RoR results were used for the 10 sccm to 75 sccm flow range. In this range, the expanded uncertainty of the RoR flow measurements ranged from 0.08 % to 0.07 % of the reading.

4.3 NIST WGFS

The Working Gas Flow Standard (WGFS) uses critical flow venturis (at 1.5 slm to 2000 slm) and laminar flow elements (at 1 sccm to 1.5 slm), to provide a reference flow value [6]. The working standards are calibrated annually with the *PVTt* or RoR standards. The WGFS has greater uncertainty than the NIST primary standards (0.1 % to 0.15 % of reading), but it is faster and makes it easier to meet the stable 100 kPa outlet pressure requirements of some customers' flow meters. The WGFS results were used for the comparison flows from 5000 sccm to 10000 sccm.

4.4 NIST dGFS

NIST owns a dGFS that is used for flow meter research. During the 10 sccm to 100 sccm tests described herein, the dGFS was used as the source of flow to the transfer standards and the *PVTt* / RoR systems, allowing three primary flow methods to be used simultaneously for the calibrations (see Figure 2).

Leak tests were conducted at NIST on the test section (including the transfer standards and associated hardware, connecting pipes and pressure tubing) by isolating the test section with valves while under vacuum and monitoring the pressure rise during several hours. Leaks were lower than 3.5×10^{-8} g/s (0.0017 sccm) when metal tubes were used to connect the flow meter to the pressure transducers instead of the plastic pressure tubes provided with the transfer standards. The pressure transducers in the molbox were tared regularly to reduce the effect of their zero drift on differential pressure measurements.

Immediately after measurements were completed by NIST, the transfer standards and related hardware were shipped back to FCP.

5 LNE Calibrations

The new dGFS for LNE was shipped to France July 2011 and was fully installed at LNE September 2011 as shown in Figure 4.

Figure 4: dGFS at LNE.

From mid-September to November 2011 two sets of calibrations were performed by LNE on each of the three transfer standards using their new dGFS.

As stated in the Introduction, this comparison was motivated by LNE's need to qualify its new dGFS, with the intent that this new standard would supersede, with reduced uncertainties, the gravimetric reference benches already in place at LNE [7]. LNE continues to use its older gravimetric calibration systems outside the range 10 sccm to 10 000 sccm with their original uncertainties. LNE now uses its dGFS between 10 sccm and 10 000 sccm with an expanded uncertainty of 0.09 % of reading + 6 x 10^{-4} mg/s from the COFRAC accreditation. However, LNE intends to apply for a lower accredited uncertainty in the future, the dGFS uncertainty of 0.06 % of reading + 3 x 10^{-4} mg/s that was used in this comparison. This uncertainty is an improvement of a factor of 2 to 3 with regard to the original LNE benches. LNE states that the metrological performance of the new standard is better due to: 1) the use of a digital comparator of higher precision; 2) the use of an automated mass handling platform to re-zero and calibrate the comparator with a mass standard without stopping the flow, thereby, minimizing the uncertainties from the drift of the balance and from the variations of ambient conditions; 3) the continuous measurement of the ambient conditions in the weighing area to calculate the air buoyancy correction to the weight of the cylinder; 4) the use of a catenary to transfer gas from the cylinder to the flow meter under test, (The catenary minimizes the effects of changing line pressure and maintains a constant force on the cylinder and balance from the downstream components.); 5) the ability to maintain a stable flow during the duration of the test due to the use of an efficient pressure regulation system on the cylinder gas line.

At the end of testing on the transfer standard artifacts in November 2011, LNE shipped the transfer standards and associated hardware to PTB in Germany.

In September 2012, LNE submitted a comparison report to COFRAC entitled “Inter-laboratory comparison of low pressure gas flow standards from 10 ml/min to 10 l/min of nitrogen”. The report included the present NIST, LNE, and PTB data and led COFRAC to grant their accreditation to the dGFS standard with uncertainty from 0.37 % to 0.09 % of reading as of January 2013. Meanwhile, the prior calibration measurement capabilities uncertainty from 0.20 % to 0.06 % of reading has been used for the comparison.

6 PTB Calibrations

In February and March of 2012, PTB used their flow standards to perform calibrations on the smaller two transfer standards. For gas flows in the range of this comparison, PTB uses two types of piston provers, one with a flow-driven mercury sealed piston (MSP) and a second with an actively-driven polymer-sealed piston (DPP) [8]. These provers measure volume flows that are traceable to SI units of length and time. Before and during each calibration, the pressure and temperature conditions were stationary. (The run-in time of the transfer standards were at least 2 h after switching on and 20 min for each flow).

6.1 PTB Mercury Sealed Prover

The MSP shown in Figure 5 was used to calibrate the transfer standard #3372. It has a full scale flow of 1000 sccm, and the MSP must be located downstream of the transfer standard because it vents to atmosphere.

The MSP has 3 tube diameters available (d_1 = 19 mm, d_2 = 44 mm, d_3= 128 mm), with the d_2 = 44 mm tube used for the comparison and a flow range from approximately 33 sccm to 1.16 slm, with an expanded uncertainty for the MSP alone of 0.25 %.

For gas flows above 10 sccm the MSPs were used because their performance is independent of the gas species and they generate interferometer velocity information that enable PTB to investigate flow instabilities caused by a meter under test.

Figure 5: Photograph of the mercury sealed piston provers (MSP) at PTB.

The inner diameters of the MSP glass tubes were calibrated by a coordinate measuring machine (CMM). In order to calibrate the diameter over its whole length, the CMM was equipped with a 450 mm long carbon fiber probe arm that was half the length of the glass tube. The CMM generated very-low-uncertainty diameter values, for example, the expanded uncertainty U = 3 µm (k = 2) for the cylinder with inner diameter of d = 44 mm and a length of l = 900 mm.

The displacement of the piston was determined by an interferometer which also detected the direction of the piston movement. The piston was driven by the flow and had to be accelerated at the beginning of measurement. This leads to a change of the pressure inside the piston prover, which also influences the pressure readings of the meter under test.

The movement of the pistons is influenced by impurities and imperfections of the inner surface of the glass tubes. This leads to velocity changes of the piston, which influences the pressure readings as well as the flow determination by the prover. This influence is a main source of flow uncertainty; the other is the average temperature of the gas at the top of the piston travel.

In order to reduce the influence of the pressure step after a start of a stroke, we waited at least 15 s before acquiring data.

6.2 PTB Dual Piston Prover

The transfer standard #3436 that has a full scale flow of 100 sccm was calibrated by PTB using the DPP located downstream of the transfer standard and venting to atmosphere. The DPP has a flow range of approximately 0.08 sccm to 112 sccm, (if used at atmospheric pressure) with an expanded uncertainty of 0.08 % of reading prior to factoring in the test point repeatability and transfer standard uncertainty applied to all participants.

A schematic of the double piston prover is shown in Figure 6. In contrast with the MSP, the pistons of the DPP generate flows by displacing volume using a stepper motor spindle drive.

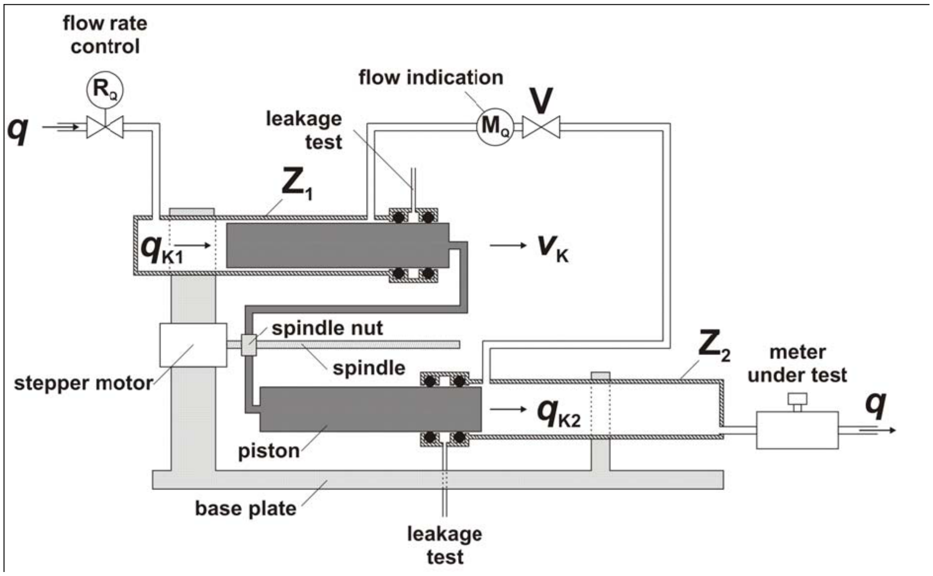


Figure 6: Schematic of actively driven double piston prover (DPP) at PTB.

In addition to generating flows, the DPP may also be used to calibrate meters under test that supply a constant flow to the DPP by means of the flow indication in the connection line between the two piston systems. If the piston systems are accelerated by the stepper motor spindle drive, the flow passing through the connection line between the two piston systems Z_1 and Z_2 decreases. This can be seen as a compensation of the gas flow q passing through the device by a mechanically generated volume displacement with opposite direction. The compensation condition is reached if zero flow inside the connection line Mq is detected. During meter calibrations, the conditions of zero flow in the connection line and stable pressure at the meter under test are applied by the data acquisition and control software.

For the transfer standard calibration, the DPP was installed downstream as a receiver of flow. After the acceleration of the pistons, the connection valve V between the two pistons was closed. Then the pressure in the piston downstream of the transfer standard was measured. The piston velocity was changed until the pressure in the system was constant during a complete stroke (Δp_{stroke} = 0.1 mbar). This was possible because of the very high flow resolution of 6×10^{-4} sccm given by the driving electronics and allowing for adjustment of the piston acceleration until the receiving rate is equal to the flow being supplied to the DPP as evidenced by the constant pressure.

The DPP was equipped with pistons with an outer diameter of 16 mm. The spindle pitch was 1 mm per revolution. Some of the main features of the DPP flow comparator are: 1) two pistons of the same diameter are realized as “fingers” which are double sealed at the end of the cylinders, 2) the pistons are mechanically coupled and will be used in order to realize simultaneous displacements (flows) with opposite signs, one cylinder/piston system is used as a source of flow and the other cylinder/piston system as a receiver of flow, 3) a flow detector and a separation valve in the connection line between the two piston/cylinder systems are used for different modes of operation, and 4) the outer diameter of the pistons and the spindle pitch are traceable to the SI unit of length.

At the end of testing in March of 2012, PTB shipped the transfer standards and associated hardware to CMI in the Czech Republic.

7 CMI Calibrations

From March to September of 2012, CMI calibrated the transfer standard artifacts using their dGFS [9, 10] shown in part in Figure 7. The theory and operational description of this dGFS are identical to that of FCP described in Section 3, above. The expanded uncertainty of CMI’s dGFS reference standard was 0.10 % of reading for all individual test points on all of the transfer standards.

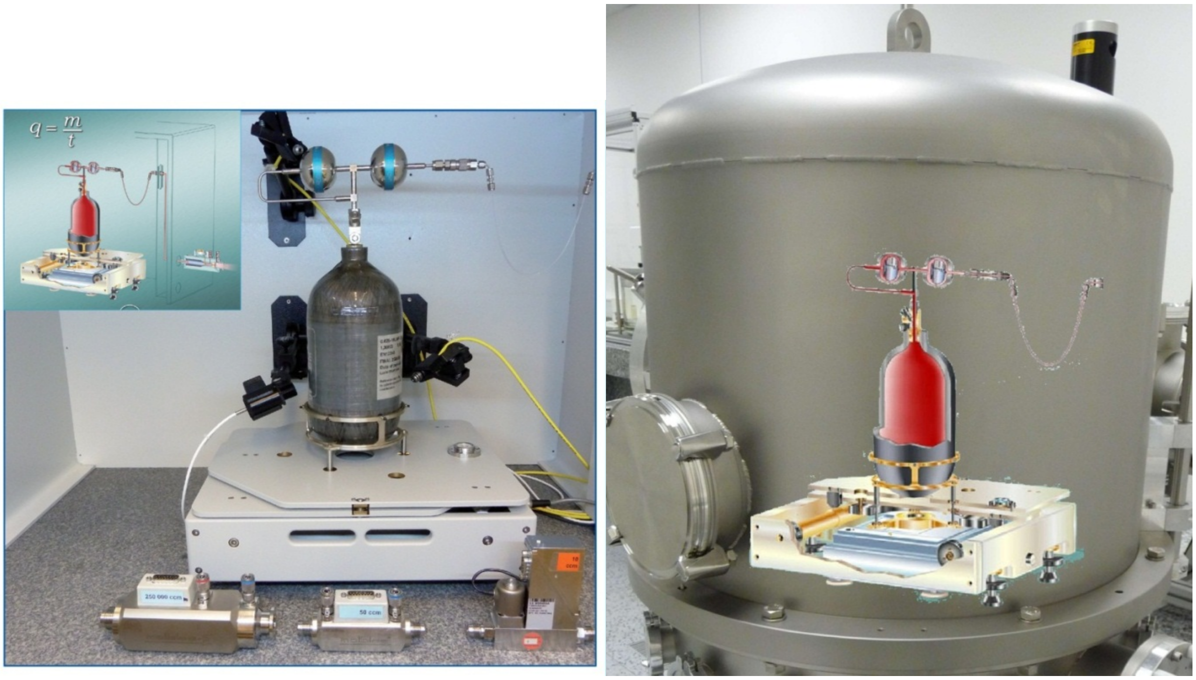


Figure 7: Composite photos of dGFS at CMI, including vacuum chamber.

Although not used for the measurements in this comparison, it is noted that CMI took an innovative and novel approach with their dGFS and has modified it to give the ability to operate with the gas cylinder, mass handler, and electronic comparator under a vacuum bell jar for weighing in a vacuum as shown in Figure 7, while maintaining the catenary connection to the flow path. Compared to operation in atmospheric conditions, when the dGFS is operated in this vacuum mode it reduces the uncertainty contributions due to buoyancy corrections to negligible values. Applying the new conditions on the uncertainty evaluation method described in [2] would yield a theoretical expanded uncertainty as low as 0.02 % ($k = 2$) of reading. However, a more realistic value of the expanded uncertainty in a vacuum that CMI is observing from practical experience is approximately 0.04 % ($k = 2$) of reading. Operation in a vacuum also prevents condensation of water on the test cylinder when the cylinder's temperature drops below the ambient dew point at higher flows. CMI also noted that the repeatability of the mass comparator improved under the vacuum.

At the end of testing by CMI in September of 2012, CMI shipped the transfer standards and associated hardware back to FCP.

8 Final Testing at FCP

During the comparison, several participants suggested that NIST or FCP perform a final calibration on the artifacts; however, such a final check was not considered to be essential or urgent for an informal comparison. Only after the consensus to publish the results was reached did FCP perform a final calibration in early January 2014.

The transfer standard artifacts were pulled out of safe storage and the calibration coefficients were verified as those used in the comparison; however, the original instrumentation for pressure and temperature measurement and flow calculation of the transfer standard elements (molbox #787) was no longer available. This particular component is designed to be interchangeable; therefore, molbox #697+ from the FCP metrology department was used instead.

As in the initial calibration, FCP used the expanded uncertainty from its ISO17025 scope of accreditation (0.10 % of reading) as the stated uncertainty of a dGFS flow measurement.

9 Comparison Calculations and Results

Participants reported the flow indicated by the transfer standard, the flow according to their reference standard, and the uncertainty of the reference standard flows. The percent difference between the transfer standard flow and the participant's reference flow was used to compare the labs. Each participant chose the number of measurements (n) collected at a flow set point and n varied between 1 and 22.

To obtain the uncertainty of the values reported by each participant, each lab's reference standard uncertainty was combined by root-sum-of-squares (RSS) with 1) the standard deviation of the mean of the *n* flow measurements at each flow set point (repeatability) and 2) the uncertainty contributed by the transfer standard due to its calibration stability over the course of the comparison.

The uncertainty contributed by the transfer standard stability, estimated to be 0.042 % ($k = 2$) of reading, is based on analysis of the calibrations performed at FCP at the beginning and end of the comparison and the two calibrations performed by LNE during the comparison. Unfortunately, the 1000 sccm #3372 transfer standard changed in calibration during transport by 0.25 % between the initial calibration at FCP and the NIST calibration. The drift was obvious because of overlapping calibration flow set points at 100 sccm and 1000 sccm using the other two molbloc transfer standards and the consistent offset observed in #3372 in all labs after the initial shipment. The transfer standards were also calibrated twice by LNE (separated by approximately 2 months). The final stability value was based on the LNE data (0.042 %) because the final FCP data (0.062 %) was performed with a different molbox after a delay of more than one year from the conclusion of the other labs' participation, and the original FCP data for the 1000 sccm transfer standard was prior to the calibration shift during the first shipment. The calibration stability values were consistent between the three transfer standards and it was decided to use the same value for all three.

The comparison reference values were calculated by the methods of Cox [11], that is, using the chi-squared consistency check and an uncertainty weighted mean of the participants' data. For the case of multiple calibrations performed at FCP and LNE, only one data set from each was used for the calculation of the reference value. However, both data sets are plotted in the following figures so that readers can view the data used to assess the transfer standard stability.

Figures 8, 9, and 10 show the difference between each participant's results and the comparison reference values for the three transfer standards. For these figures, the participant's results have been purposely offset along the flow axis so that they do not overlap to make them easier to visually discern from each other. The horizontal line at $y = 0$ represents the comparison reference value and it has an uncertainty ranging from 0.036 % to 0.052 % in this comparison. The error bars are the 95 % confidence level RSS of the reference standard, repeatability, and transfer standard uncertainties. Error bars crossing the $y = 0$ line indicate agreement of a participant's results with the comparison reference value within uncertainty expectations, which was the case for all labs at all flows in this comparison.

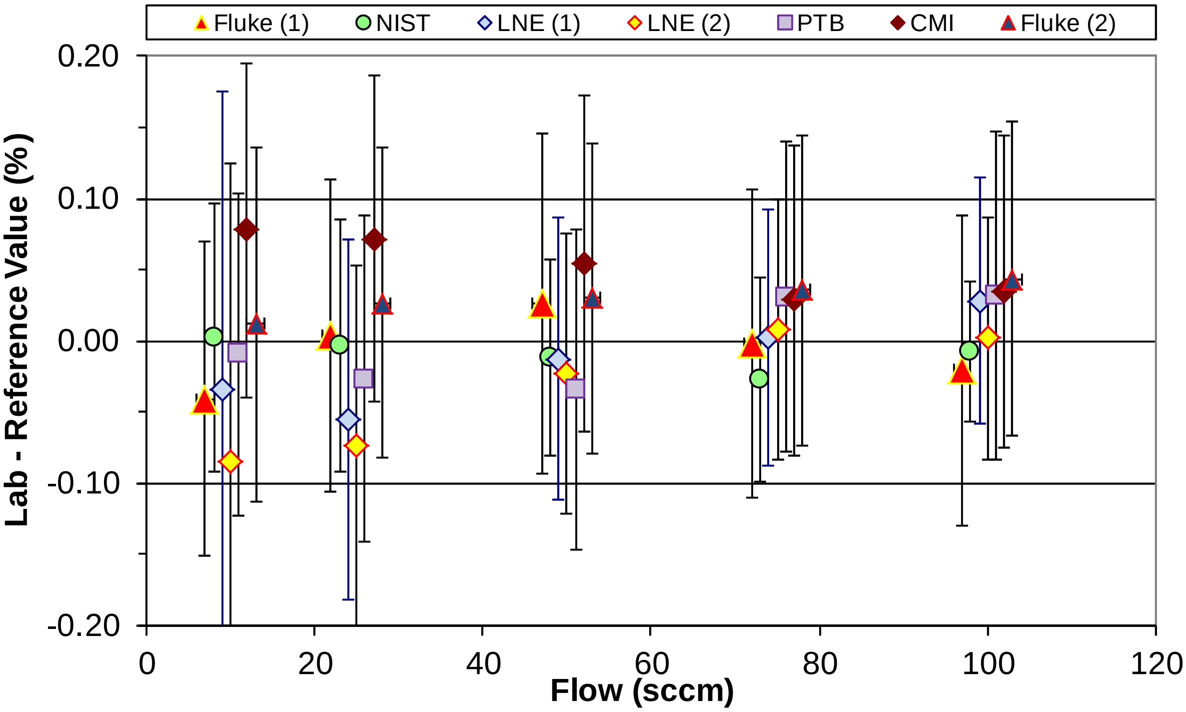
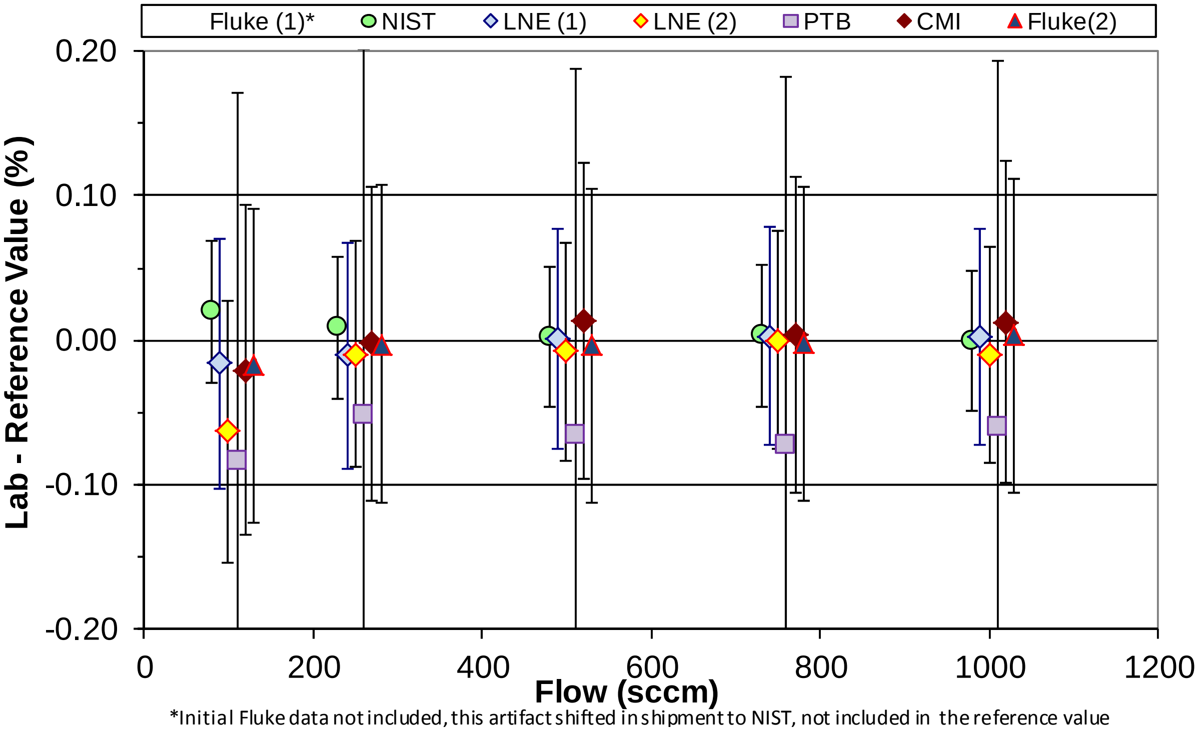


Figure 8: Comparison results for the 100 sccm artifact SN 3436.



*Initial Fluke data not included, this artifact shifted in shipment to NIST, not included in the reference value

Figure 9: Comparison results for the 1000 sccm artifact SN 3372.

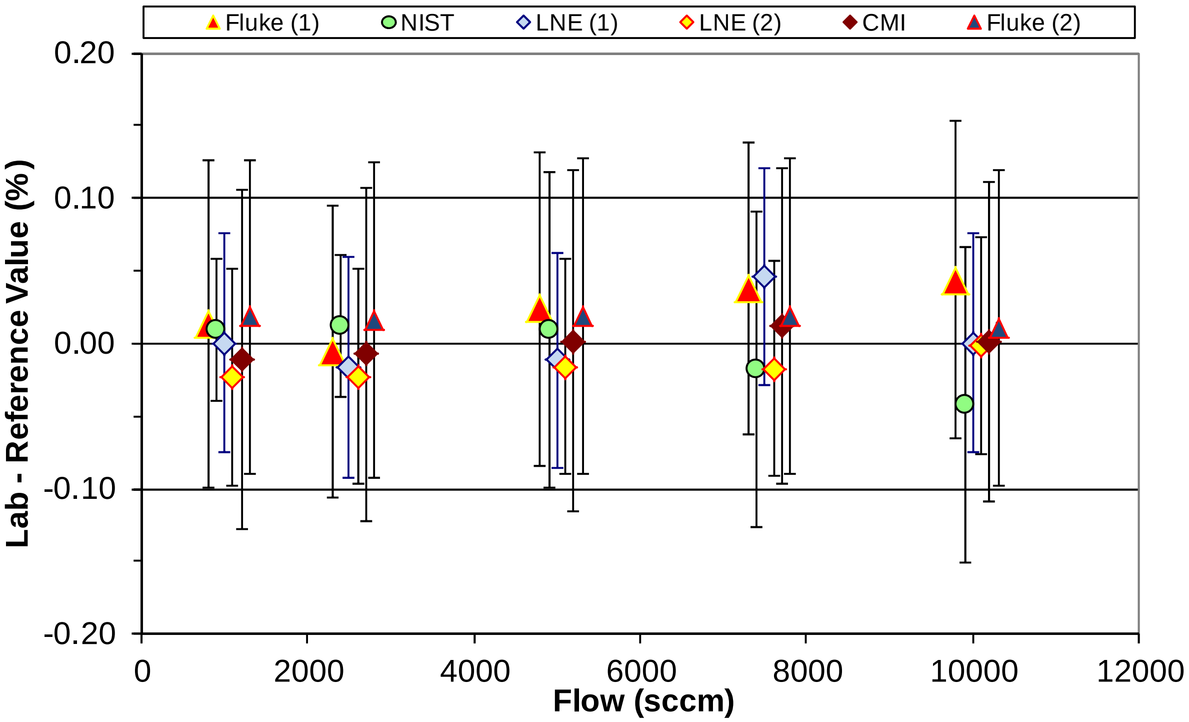
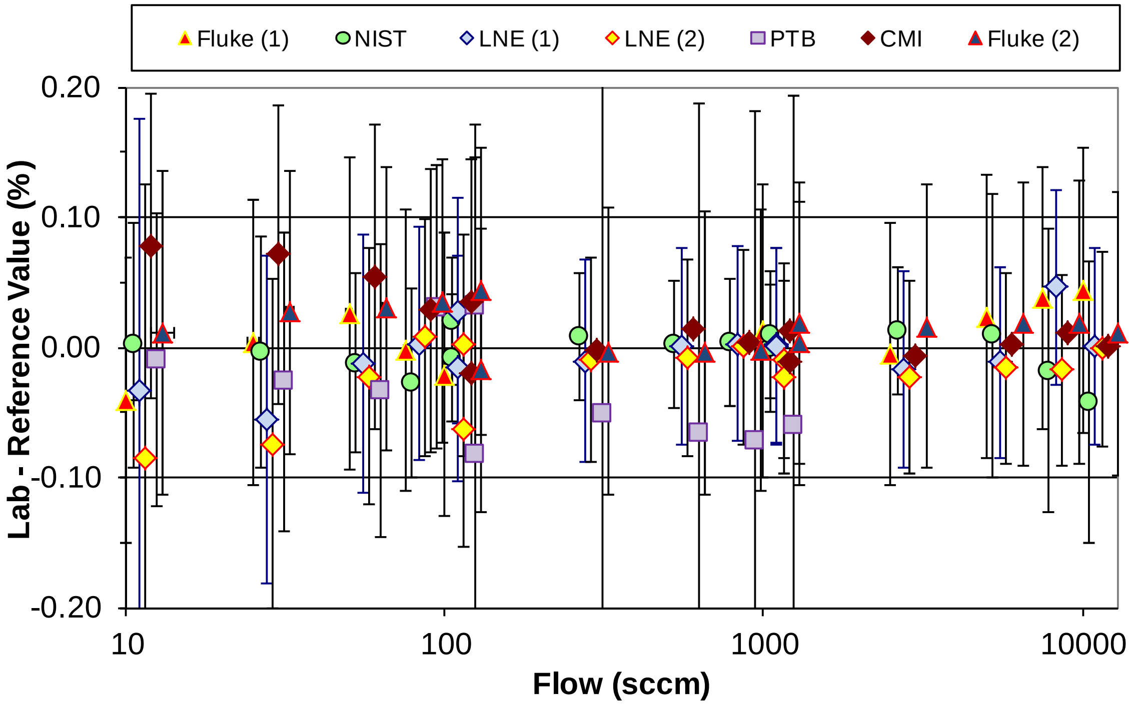


Figure 10: Comparison results for the 10000 sccm artifact SN 3410.



Error! Reference source not found.. Log-scaled plot of the results for all three transfer standards at all measured flows.

Figure 11 is a log-scaled plot of the results for all three transfer standards at all measured flows. For flows near 100 sccm and 1000 sccm, two transfer standards were used at the same flow (on different occasions). The data taken with the pairs of transfer standards are in good agreement: excluding PTB (due to the uncertainty difference between the two references used and no data taken on the 10 000 sccm transfer standard), the largest difference at 100 sccm was 0.065 % and the largest difference at 1000 sccm was 0.023%.

10 NIST Internal Comparison Results

As explained in section 4, four NIST flow references were used (*PVTt*, RoR, WGFS, and dGFS), but only a portion of those data were used in calculating the comparison reference values and are shown in the figures above. Figure 12 plots the degrees of equivalence for all of the data collected with the four NIST flow references. The agreement with the comparison reference values is within 0.047 % and well within uncertainty expectations (i.e. all error bars cross $y = 0$). The largest difference between any two NIST results was 0.075 % at 10 000 sccm and is probably due to temperature effects on the critical flow venturis used in the WGFS. The largest difference between any two flow references observed during simultaneous calibrations using the *PVTt*, RoR, and dGFS standards between 10 sccm and 100 sccm (see Figure 2) was 0.045 %. The $|E_n|$ values for the data in Figure 12 are ≤ 0.63, indicating that all four standards are operating within their uncertainty claims.

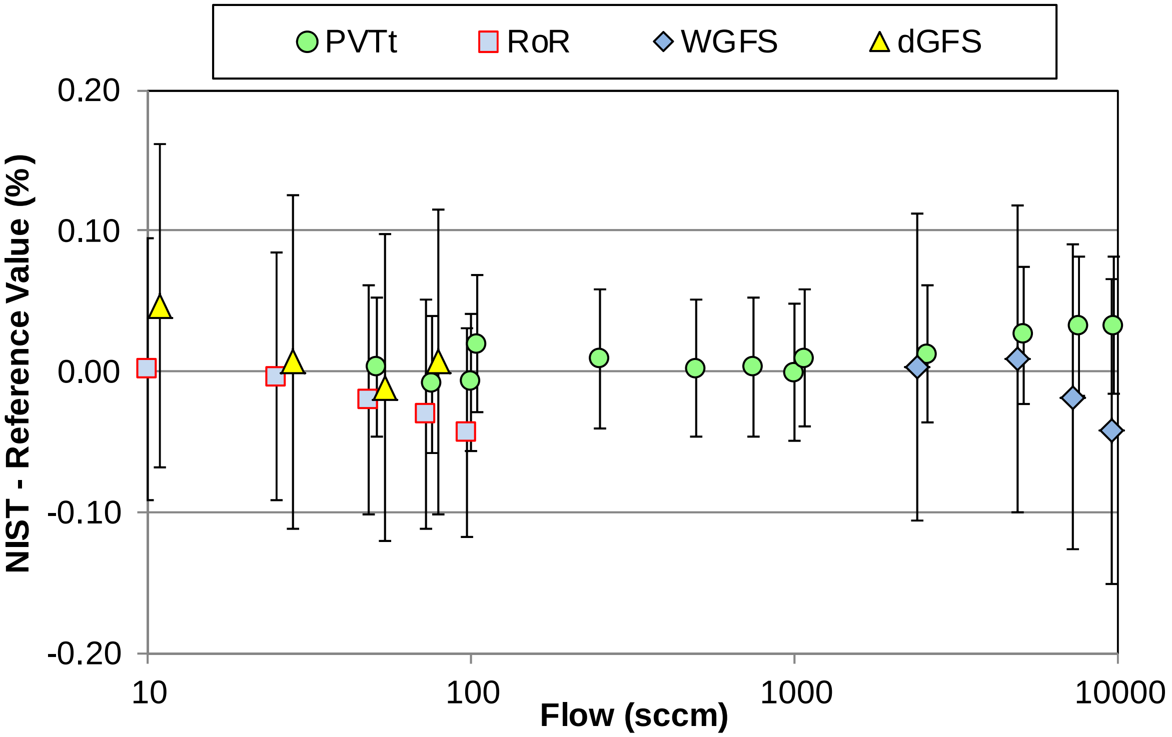


Figure 12. Degrees of equivalence for the four NIST flow references.

11 Conclusions

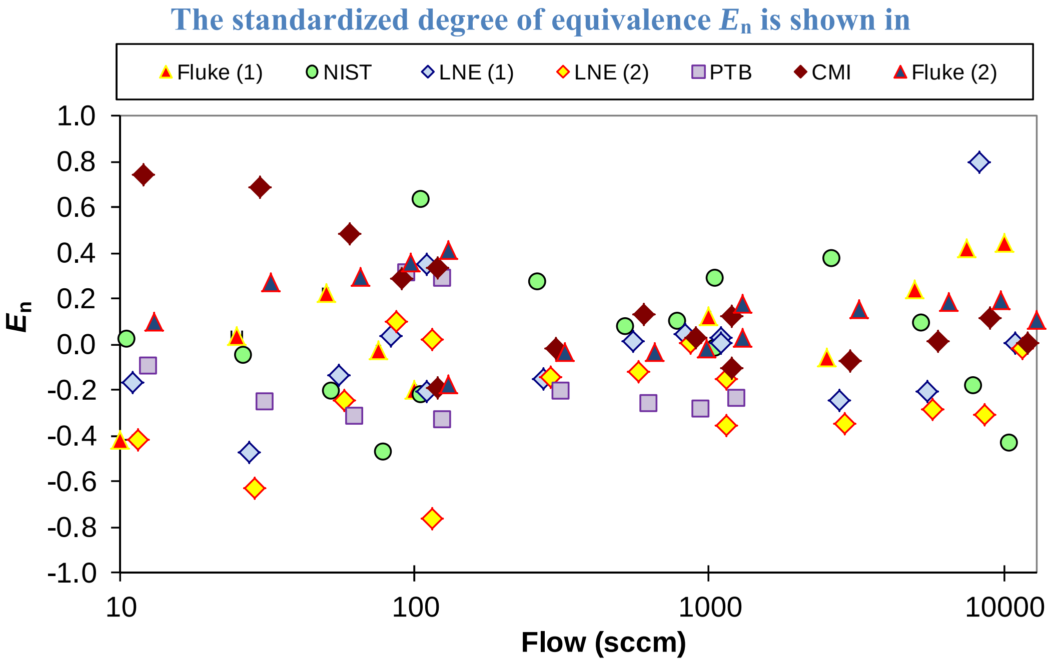


Figure 113. E_n is the difference between the participants' result and the comparison reference value divided by the uncertainty of this difference:

$$E_n = \frac{x_i - x_{\mathrm{ref}}}{\sqrt{U^2(x_i) - U^2(x_{\mathrm{ref}})}}. \qquad (3)$$

For a transfer standard with low uncertainty, $|E_n|$ values < 1 indicate results within a lab's uncertainty specification. All values in this comparison were 0.8 or less showing acceptable results for all participants.

For this comparison, x_{ref} was not determined by one reference lab, but is the uncertainty weighted average of the participants' results given by equation 1 in Cox [11]. $U(x_{\mathrm{ref}})$ is the expanded uncertainty of x_{ref} which is given by equation 2 of Cox [11] (multiplied by a coverage factor of 2). $U(x_i)$ is the expanded uncertainty of the participant's reported result x_i and this uncertainty includes 1) the laboratory's reference standard uncertainty, 2) repeatability or reproducibility of the *n* measurements made in each lab, and 3) the uncertainty introduced by the transfer standard. The ratio of the uncertainty contributed by the transfer standard to the minimum participating lab uncertainty is 0.042 % / 0.025 % = 1.68. Since the participant's expanded uncertainty was used in the calculation of the reference value uncertainty (in equation 2 of Cox [11]), the $U(x_{\mathrm{ref}})$ is subtracted from the $U(x_i)$ in the denominator of Eq. 3.

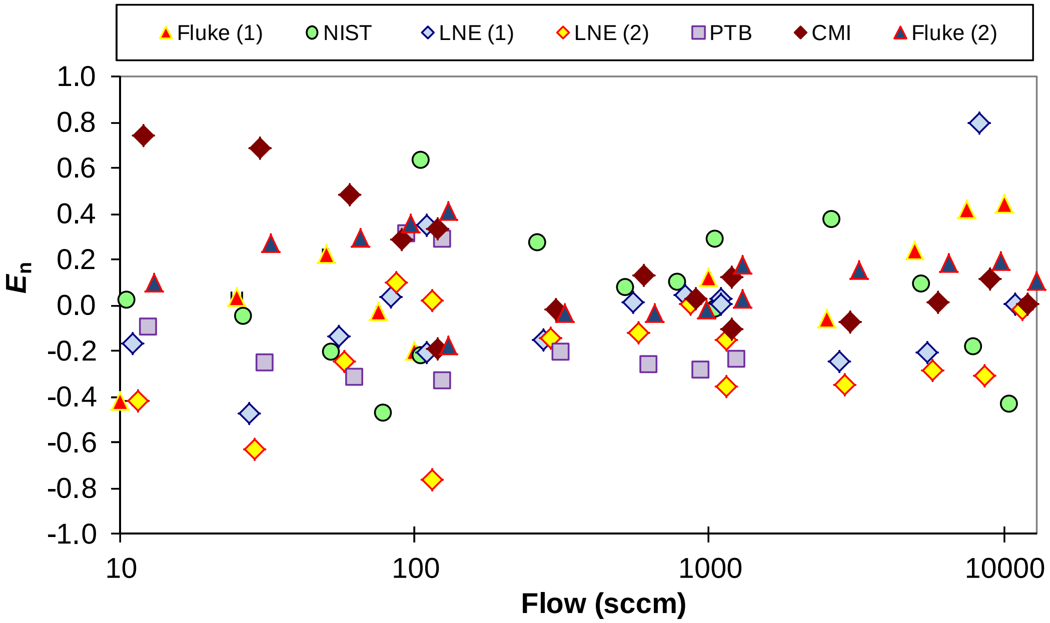


Figure 113: Standardized degrees of equivalence │ En │ versus flow for the comparison.

12 Future Work

Because of the satisfactory results of this comparison, a new comparison is being established in 2014 to assist dGFS users in extending the validated flow range below 10 sccm and above 10 000 sccm with acceptable uncertainties.

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