SWISS PRIMARY VOLUMETRIC STANDARD FOR LOW GAS FLOWS: EXPERIENCES AND PROGRESS

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Summary

In 1994 the Swiss Federal Office of Metrology and Accreditation (METAS) purchased a commercial volumetric calibration system for low gas flows. The main task of the instrument is to establish the traceability of inert gas flow measurement results for immission calibration methods such as dynamic dilution or dynamic generation of calibration gases by means of permeation tubes.
During characterisation it became clear, that several modifications of the instrument were necessary to fulfil the must requirement of 0,2 % relative expanded measurement uncertainty. The details of the modifications, an actual uncertainty evaluation and first results of recent comparisons are shown.

Résumé

L'Office fédéral de métrologie et d'accréditation (METAS) a acquis en 1994 un système commercial qui doit assurer la traçabilité de résultats de mesures de petits débits de gaz inertes. Ces résultats interviennent entre autres dans le titre de mélanges étalons de gaz fabriqués par dilution dynamique ou par génération dynamique de mélange gazeux avec des tubes à perméation. De tels mélanges sont utilisés lors d'étalonnage d'instrument destinés aux mesures d'immissions de polluants gazeux.
Une incertitude élargie de mesure de 0.2 % relatif était exigée. Pour atteindre cet objectif, d'importantes modifications ont du être apportées au système initial. Les détails de ces modifications, une évaluation de l'incertitude actuelle du système et les premiers résultats de récentes intercomparaisons sont présentés.

1 Introduction

The need for measurements of low gas flows with low uncertainties comes on one hand mainly from the immission measuring community where dynamic mixing and preparation of calibration gases is important [1, 2]. On the other hand also semiconductor industry as well as chemical and medical applications utilise high accuracy gas flow measurements and calibrations.

For these reasons Swiss Federal Office of Metrology and Accreditation (METAS) decided to set up a calibration system for flows in the range from 1 cm^3/min to 30 dm^3/min @ standard temperature and pressure [3]. Starting with a commercial volumeter there were several problems with different components that were responsible for the non-conformity to the specified relative uncertainty of 0,2 %.

Various steps of reengineering were necessary to bring the complete system to a level of a 'primary' calibration facility which is traceable to the International System of units (SI) via calibration of the components with standards at METAS.

2 The primary volumeter

The primary volumetric standard (Figure 1) consists of a set of three precision machined glass cylinders. In these cylinders mercury sealed pistons are raised by inflowing inert and dry gas. From the continuously measured difference in height (Δh) of the raising piston by diode laser interferometry and the elapsed time (Δt) the velocity of the piston results. Multiplying the velocity of the piston with the mean inner area of cross section ($D^2 \cdot \pi/4$) of the tube the volume flow is given. The gas volume flow (q_V) at reference conditions (T_s, p_s) is then calculated according to equation (1) with the measured gas temperature (T_g) and gas pressure

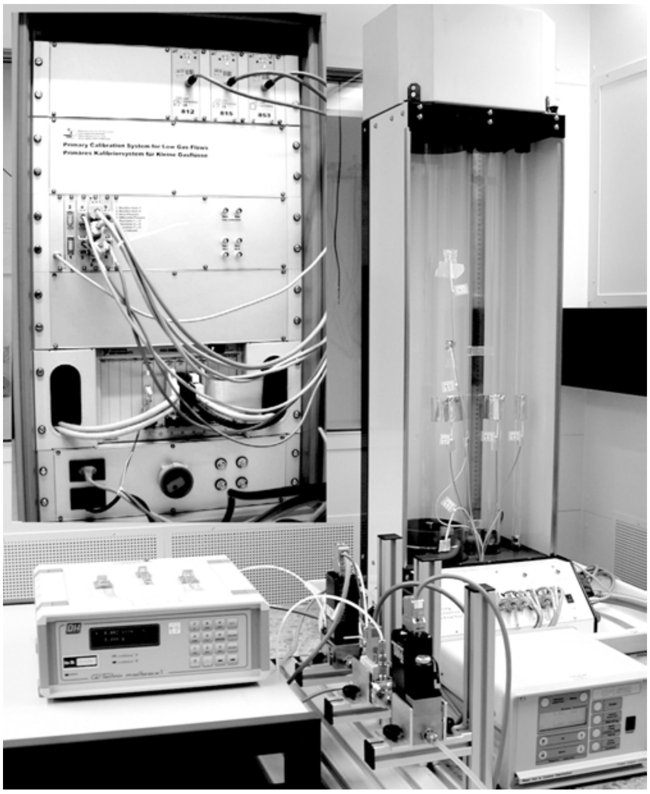

Figure 1: Picture of primary volumeter for low gas flows at METAS with separate electronics

below the piston (p_g) assuming ideal behaviour of the measured gas.

$$q_V = \frac{D^2 \cdot \pi}{4} \cdot \frac{\Delta h}{\Delta t} \cdot \frac{p_g \cdot \mathrm{T_s}}{\mathrm{p_s} \cdot T_g} \qquad (1)$$

The volumeter is located in an air conditioned measurement chamber (20,0 ± 0,1) °C, separated from all electronic equipment and with the possibility to measure in the dark.

2.1 Components in detail

Electronics and software Data acquisition had to be completely redesigned due to a lot of new requirements for the reengineered system and due to poor documentation of the original electronics. It is now done by a standard PXI system from National Instruments™ using counter/timer, digital I/O, multifunction and high-precision temperature modules and an MXI-3 connection to Windows PC for software control. The software allowing automatic measurement procedures was developed under LabVIEW® at METAS and is fully open and transparent due to graphical programming.

Glass tubes The three original glass tubes have a length of 1 m and an inner diameter of 143,714 mm, 44,463 mm and 12,695 mm. They were calibrated using a 3-D measuring machine that is traceable to the Swiss length standard. The relative experimental standard deviations of the inner diameters along the tubes are $9 \cdot 10^{-5}$ for the big, $1{,}3 \cdot 10^{-5}$ for the medium and $1{,}4 \cdot 10^{-4}$ for the small tube. The calibrations at METAS are consistent with the initial calibration done with an air plug calibration tool using NIST-traceable ring gauges as references.

Position measuring device The first measuring system for the height difference measurement of the piston consisted of three ultrasonic sensors. The reflector area was an aluminium plate placed on the pistons. The resolution was about 1,3 mm caused by time resolution for the evaluation of reflected sound signal. This system has been shown to be poor in linearity specially for the big and the small tube. There was a clear saw tooth shape of the ultrasonic signal versus an interferometer signal parallel to the measuring path with a non-linearity of about 1 % except for the medium tube. For this reason and because external calibration was troublesome we changed to an OEM-version of a miniaturised diode laser interferometer HC-250 from CSO. A 4 mm glass sphere coated on the lower spherical cap with gold is used as a reflector in the centre of the pistons. The vacuum wavelength of the interferometers is online corrected for temperature and pressure according to [4] and regularly calibrated and adjusted via a calibration of the distance measurement with a laser interferometer traceable to the Swiss length standard. The raw signals from the HC-250 electronics are evaluated with two 32-bit-counters of a PXI-6602 counter/timer module supplying the number of counts and the direction of the moving reflector. Particular mechanical supports were made for the position adjustment of the interferometers and the positioning of the reflectors on the upper surface centre of the pistons. The resolution of the diode laser is 100 nm and therefore it can also be used for the leak check procedure of the entire system.

Time measurement Time difference is now measured with a 32-bit-counter of the PXI-6602 counter/timer module. It is calibrated using a SRS counter/timer traceable to the Swiss time standard. An important figure is the standard deviation of the time difference between the position acquisition and the time acquisition. It is smaller than 130 µs on a difference of 2,3 ms between two subsequent acquisitions.

Temperature measurement The initial PT-100 sensor gave a very stable reading of the inflowing gas with a resolution of 0,1 K. Unfortunately the sensor was affected by heat transfer via the brass support wherein he was placed and the most representative spot to measure temperature is just not the gas inlet. Moreover the brass support was heated during measurements by two electromagnetic valves mounted nearby. Gradients of up to 0,7 K could be observed between inflowing gas and glass surface caused by irradiation and heating of the valves. Therefore we changed the temperature sensor to nine super stable YSI™ NTC thermistors 46007 (5 kΩ @ 25 °C) with stable current supply (25 µA) and voltage measurement provided by a NI 4351 module. They are calibrated against a 25 Ω platinum resistance temperature detector traceable to Swiss temperature standard and serve also to characterise temperature profiles. Temperature for referencing is taken on the glass surface of the respective tube assuming that there is an important heat exchange between the measurement gas and the inner glass surface of the tube during one measurement run. The resolution of the sensor readings is 1 mK.

Pressure measurements The sum of two individual pressure sensors, an absolute ambient pressure sensor and a differential pressure sensor was used for referring to reference conditions ($\mathrm{T_s}$, $\mathrm{p_s}$) in the commercial instrument. To minimise the uncertainty we now measure the absolute pressure below the pistons with a quartz resonance sensor RPT 200 from DRUCK calibrated against the Swiss pressure standard. The differential sensor has been kept for security reasons to open bypass valves in case of too high counter-pressure caused i.e. by piston friction.

Pneumatics For the above mentioned problems with valve heating affecting temperature measurement the pneumatic part was completely changed from a electromagnetically driven one to a pneumatically driven one. Special care has been taken also to the selection of tube cross sections to avoid on the one hand counter pressures caused by restrictions at maximum flows and to reduce on the other hand the dead volumes for the minimum flows.

2.2 Characterisation

As an example a characterisation experiment can be shown, for which the experimental setup is outlined in Figure 2. A fully automatic procedure has been run overnight with the same flow on two different tubes measured with both the primary volumetric system and the commercial secondary standard molbox™/molbloc™.

1 Gas supply
2 Dual stage pressure regulator
3 Shut-off-valve
4 Particle filter
5 Electronic pressure regulator
6 Control device for (5)
7 Molbloc
8 Molbox1
9 Mass flow controller
10 Primary volumetric flow standard (PVFS)
11 Electronics for PVFS
12 Personal Computer

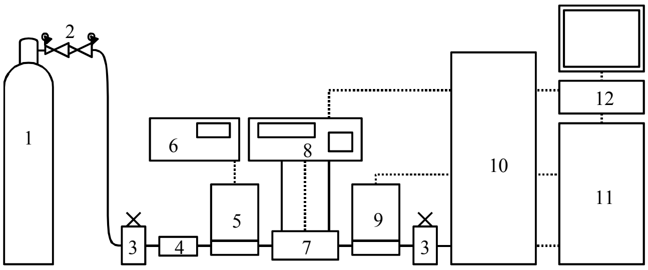

Figure 2: Experimental setup for characterisation

The measurement points in Figure 3 referring to the secondary ordinate are means of four measurement runs during for about 30 minutes. So the complete procedure took more than seven hours. The points with odd measurement numbers were carried out on the big tube, the even ones on the medium tube.

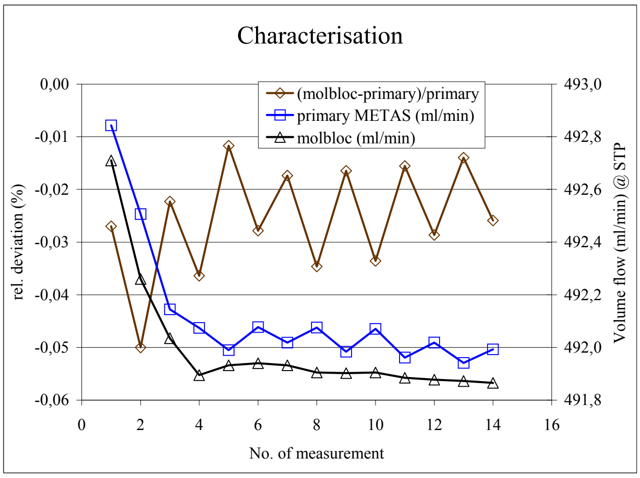

Figure 3: Results of characterisation experiment

As outcome of such an experiment several important items can be mentioned. First there is information about the stability of the flow generation done with a mass flow controller. As the reading of the molbloc and the primary system correlate firmly it is clear that for the first three points the flow was not jet ideally stable but afterwards it stays within $2 \cdot 10^{-4}$ of the volume flow during over more than five hours. Looking at the standard deviation of the difference between one tube and the molbloc the repeatability of the molbloc and the primary system can be evaluated as better than $5 \cdot 10^{-5}$. Secondly a mean difference between the big and the medium tube for the primary system can be calculated. This unknown systematic deviation can be interpreted as a inter-tube reproducibility an its value is $1{,}5 \cdot 10^{-4}$ of the flow. Finally the initial gravimetric calibration of the molbloc which dates from October 1997 was excellent in this case, because the mean relative deviation compared to the primary standard is $2{,}4 \cdot 10^{-4}$ which is far below the expanded uncertainty specifications for molbloc measurements of 0,2 %.

2.3 Uncertainty evaluation

For the estimation of the combined standard uncertainty we applied the equation (1) as model equation for a program called GUM workbench [5]. The various uncertainty contributions of the input variables are treated according to the rules of ISO GUM [6]. The Table 1 shows an example of the uncertainty budget for 500 cm^3/min. For every other flow measured on the primary system a similar budget based on the respective measurements can be calculated.

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Sensitivity Coefficient	Index
D_{korr}	44.4625 mm	0.0030 mm			
π	3.14159				
Δ_h	608.344 mm	0.030 mm	50	0.822	1.5 %
Δ_t	99.0905 s	0.0049 s	50	-5.05	1.5 %
p_d	95.200 kPa	0.015 kPa	50	0.00525	15.1 %
$\mathrm{p_s}$	101.325 kPa				
$\mathrm{T_s}$	273.15 K				
T_g	293.56 K	0.10 K	50	-1.70	70.7 %
D	44.4625 mm	$0.13 \cdot 10^{-3}$ mm	18	22.5	0.0 %
K_D	0.0 mm	0.0030 mm	50	22.5	11.1 %
q_V	500.0ml/min	0.203 ml/min	93		

Quantity: q_V
Value: 500.00 ml/min
Relative Expanded Uncertainty: ±0.081 %
Coverage Factor: 2.0
Coverage: 95.45%

Table 1. Uncertainty budget for a typical example for the primary standard at METAS

D_{korr} is the sum of mean inner diameter D and a correction K_D with an important uncertainty originating from the calibration standard and the respective calibration procedure. For Δt and Δh the relative standard uncertainty is $5 \cdot 10^{-5}$ because for conditions $\Delta t > 30$ s and $\Delta h > 300$ mm the specification of the stability of the quartz and the laser diode become predominant contributions for the uncertainty of these two input variables. For the gas pressure uncertainty the non ideal measurement site and possible back pressures for bigger flows dominate the contributions from calibration and stability of the sensor. The same is valid for the gas temperature where gradients (T_{max}-$T_{min} < 0{,}1$ K) are tested with an inline temperature measurement. The calibration (0,02 K) and stability (0,01 K) uncertainties are minor contributions to the combined temperature uncertainty. Uncertainty components such as non-ideal behaviour of the measured gas and gas impurities have been considered to be negligible.

Together with the reproducibility specification of an ideal instrument as i. e. a molbloc of 0,1 % the combined general uncertainty statement for a molbloc calibration is 0,13 % relative expanded uncertainty for measurements with the big and the medium tube and 0,25 % for the small tube.

3 Comparisons

First intercomparisons have already been performed with a intermediate state of the primary volumeter for low flows and they were reported in [7]. Most recent comparisons with a primary dynamic gravimetric system at BNM-LNE are not yet published. In an indirect comparison via a molbox / molbloc system the two primary systems with independent traceability to the SI agreed within 0,1 % in the range between 10 cm^3/min and 10 dm^3/min and within

0,4 % from 3 to 10 cm^3/min. Furthermore there was very good concordance of the stated uncertainties.

4 Conclusions

The METAS primary volumetric calibration system has been taken as an example to show that there are commercial systems which have difficulties to comply with the specified expanded uncertainty. With a remarkable technical effort it was possible to keep and even exceed our initial target uncertainty of 0,2 %. International comparisons show that the measured differences between primary standards of any measurement principle are in excellent agreement with the given measurement uncertainties. For the future one should put emphasis also on the comparison of other gases than nitrogen, to improve knowledge of potential transfer standards and to extend the measurement range to flows below 10 cm^3/min.

5 Acknowledgments

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The use of firm, brand, and trade names in this paper is for identification purposes only and does not constitute any endorsement.

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