Final report
Results and evaluation of key comparison CCM.P-K12.1 for very low helium flow rates (leak rates)

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CONTENT

1. Introduction

The Czech Metrology Institute (CMI) took part and failed to prove equivalence in the Key Comparison CCM.P-K12 of helium leak artefacts (leak rates) into vacuum [1].

CMI used a method of comparison of He flow from the constant pressure – variable volume flowmeters and from the transfer standard. A quadrupole mass spectrometer (QMS) Prisma QMA 200 served as a comparator. The failure was caused by an atmospheric leak through a valve. Manipulation with this leaking valve significantly changed the concentrations of atmospheric gases in the chamber. He signal depends on the partial pressures of other present gases. Nitrogen and oxygen levels stabilised quickly, but water remained unstable even after 20 min.

As a solution (except changing the valve), CMI vacuum laboratory lowered the emission current of QMS from nominal 2 mA to (0.1 – 0.4) mA. The dependence of the He signal on the residual atmosphere is weaker by the lower emission currents. Hence it has a better short-time stability to serve as a He flow-rates comparator. Further, a lower partial pressure of water is reached by opening a by-pass parallel to the orifice. Both precautions increase a relative noise of the He signal. Hence it is necessary to use the longer integration times (cca 5 s for the lowest leak rates). However, the resultant total uncertainty is lower than originally.

The Institute of Metals and Technology (IMT), a successful participant in CCM.P-K12, volunteered to serve as pilot and link in a following bilateral comparison of IMT and CMI that obtained designation CCM.P-K12.1 in June 2012. It was decided to perform the comparison with a glass permeation helium leak artefact at nominally $3 \cdot 10^{-11}$ mol/s ($7.4 \cdot 10^{-7}$ mbar·L·s^{-1}) at 23 °C. The comparison measurements were performed in October 2012.

2. Transfer standards and quantity to be determined

The helium permeation leak Alcatel – FV4300, serial No. FC07 000 676 served as the transfer standard. Its nominal leak rate at 20 °C by time of purchase in 2007 equalled $2.7 \cdot 10^{-11}$ mol/s ($6.7 \cdot 10^{-7}$ mbar·L·s^{-1}) and its nominal temperature coefficient equals +3 %/K. The leak was equipped with a KF16 flange and a valve. The valve was left open during transportation to minimize the accumulation of helium gas downstream of the permeation leak element. This kept the density of helium in the permeating part roughly constant during transportation. This was important in order to have acceptable time constants for reaching equilibrium after installation in a laboratory. For transport, the connecting flange was equipped by a protective plastic cover leaving it more or less open to atmosphere.

The measurand determined by each laboratory was the molar flow rate of the helium atoms flowing out of the transfer standard leak at the time of calibration:

$$q_\nu = \frac{\Delta \nu}{\Delta t} \text{ test leak at 23.0 °C,} \tag{1}$$

where $\Delta \nu$ is the number of moles of helium exiting out of the leak in the time Δt.

This quantity depends on the temperature of the leak artefact. For this reason the target temperature was (23.0 ± 0.2) °C. This could not be always followed, but all the values taken at a temperature different from 23.0 °C were recalculated to values which would have been measured at 23.0 °C exactly. This was done by applying a measured temperature coefficient of the leak.

Since the flow from the transfer standard leaks was permanent and the gas reservoir limited, q_ν could also be time dependent. But this effect could be neglected thanks to the short time needed for this comparison.

The molar flow was not measured directly, but the known “energetic” throughputs q_{pV} [2] at some thermodynamic temperature T were converted from q_{pV} into q_ν by:

$$q_\nu = \frac{q_{pV}}{RT}, \tag{2}$$

where R =8.3145 Pa·m³·mol^{-1}·K^{-1} is the universal gas constant.

3. Participating laboratories and their measurement systems

The only participants in this comparison were IMT - Slovenia (pilot) and CMI - Czech Republic. Both their laboratory standards took part in CCM.P-K12 and were considered as primary [1].

3.1. CMI

The CMI used a comparison method with a constant pressure flowmeter. A quadrupole mass spectrometer (QMS, Balzers Prisma) installed at the calibration chamber of a continuous expansion system [3] to [7] served as indicator to compare the helium gas flows from the flow meter (signal on QMS: I_2) and from the transfer standard leak (signal on QMS: I_1), which were intermittently admitted into the calibration chamber, see Fig. 1.

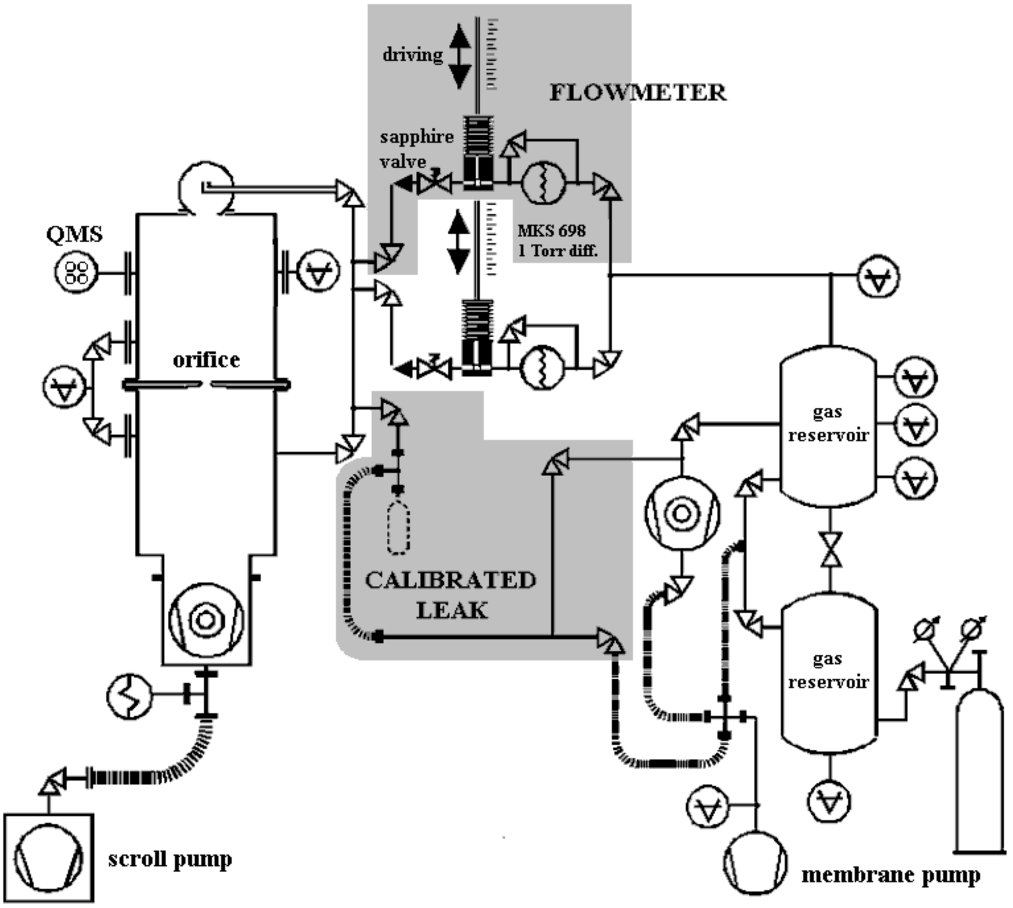

Figure 1 Schematic of CMI set-up

The calibrated leak was connected to an auxiliary turbomolecular pump (backed by a membrane pump) in the periods when it was not connected to the calibration chamber. The linearity of the QMS was checked in the relevant range of this comparison. The non-linearity was found to be insignificant. Nevertheless the gas flow from the flowmeter was set by the sapphire valve so to give a partial pressure signal as close as possible to the signal caused by the transfer standard. The molar flow rate from the leak under calibration is given by

$$q_{\nu,\mathrm{leak}} = \frac{I_1}{I_2} q_{\nu,\mathrm{FM}} \qquad \frac{I_1}{I_2} \approx 1 \ , \tag{3}$$

where $I_{1,2}$ are offset corrected readings. The offset reading is obtained when there is no helium flow onto the QMS.

No thermal bath was utilised to stabilize the temperature of the transfer standards. Instead, they were thermally insulated by the means of a foam wrap. Its temperature was measured by two sensors Pt1000 fixed to its reservoir container and the mean of their indications was taken into account. The temperature of the transfer standard remained stable within ±0.1 °C.

3.2. IMT

The IMT has developed a primary helium leak [8] based on a glass permeation element, a reservoir with adjustable helium gas pressure and a calibration facility for in-situ measurement of generated helium gas flow by a pressure rise method using spinning rotor gauge, see Fig. 2.

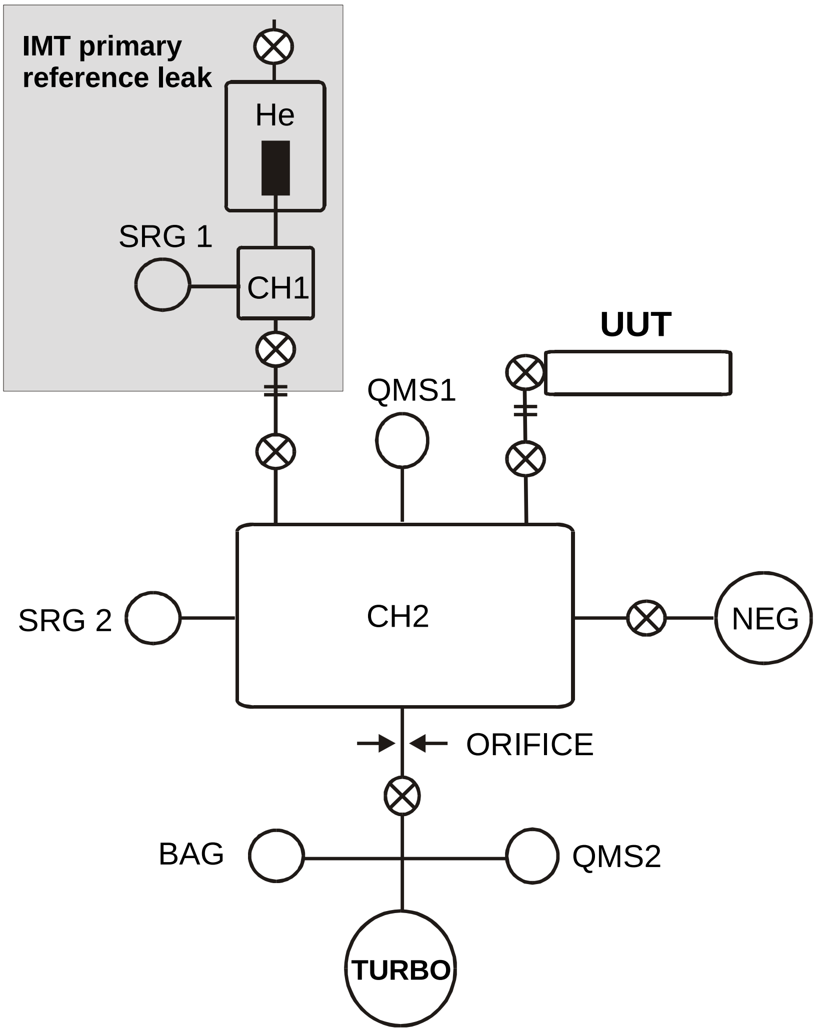

Figure 2 The IMT leak calibration/comparison system

The fill pressure in the reservoir can be varied from 100 Pa to 1 MPa, to generate flows from 10^{-15} mol/s to 10^{-11} mol/s with the glass permeation element at room temperature. Compared to the description in [8] some improvements were made, e.g. a temperature shroud made of Al with a possibility to heat the helium reservoir with the glass permeation element to 140 °C, Ti/Ta getter was replaced with ST 122 NEG from SAES Getters.

This primary helium leak is connected to a leak comparator apparatus shown in Fig. 2. The He partial pressure in the comparator vacuum chamber (CH2) is measured with a quadrupole mass spectrometer (QMS1). The He gas pressure in the reservoir of the primary leak is adjusted to produce nearly the same He signal as the unit under test (UUT).

The volume of the comparator vacuum chamber was also determined. This enables direct primary measurement of He gas flow from UUT (the transfer standard) by pressure rise method in CH2 (nominal volume 7 L) using SRG 2 (traceable to PTB). The purity of accumulated helium gas can be checked by another quadrupole mass spectrometer (QMS2). This method is generally used for He flows from 10^{-13} mol/s to $3 \cdot 10^{-9}$ mol/s, and was applied in this comparison.

4. Chronology and measurement procedure

In order to determine the stability of the transfer standard, it was decided that two measurement series will be made by CMI, prior and after the measurements at IMT. Tab. 1 presents the actual chronology of the calibrations. Each laboratory was required to perform 6 measurements on the first calibration day and to repeat this series on the second day.

Table 1 Chronology of measurements. CMI1 and CMI2 mean the 1st and 2nd calibration sequence carried out by CMI.

Laboratory	Measurement
CMI1	2012-10-03 and 2012-10-04
IMT	2012-10-10 and 2012-10-11
CMI2	2012-10-15 and 2012-10-16

5. Uncertainties of reference standards

The Type B uncertainty of IMT was 0.49 % (for $k = 1$) and of CMI from 1.52 to 1.54 % (for $k = 1$). Type A uncertainties will show up in the scatter of data at repeat measurements, and were calculated using methods described in Sec. 6 and 7.

6. Results of the pilot laboratory (IMT)

6.1. Temperature coefficient of transfer standard leak

To correct the data obtained at different temperatures to a common reference temperature, the temperature coefficients of the flow rate from the leak artefact had to be determined. It was done from the comparison data plus some extra preliminary measurements. A linear least square fit was applied to the data to determine the slope as relative temperature coefficient α_T of the flow rates:

$$\alpha_T := \frac{\Delta q_v}{q_v(23°\mathrm{C})\Delta T} = (2.61 \pm 0.05)\ \text{\%/K}. \tag{4}$$

To correct the measured leak rates to a common temperature of 23 °C, the following formula was applied:

$$q_{v,j}(23°\mathrm{C}) = q_{v,j}(T_j) / \left(1 + \alpha_T (T_j - 296.15)\right). \tag{5}$$

Herein $q_{v,j}$ is the leak rate as determined by participant j for the temperature T_j in kelvins at the time of calibration.

6.2. Results of IMT (pilot)

The results of the pilot are summarized in Tab. 2. In each row the calibration date and time, the mean temperature ϑ of the leak, the mean measured leak rate $q_{\mathrm{v}}(\vartheta)$ at this temperature, the uncertainty of the used standard u_{et} ($k = 1$) as the main part of the Type B uncertainty and the molar flow rate q_{v}(23 °C) calculated by Eq. (5) are given. After each day the mean and the standard deviation of the mean u_{A} of ϑ, $q_{\mathrm{v}}(\vartheta)$ and q_{v}(23 °C) are stated. The value of u_{A} was calculated by

$$u_{\mathrm{A}} = \sqrt{\frac{1}{N(N-1)} \sum_{l=1}^{N} \left(q_{v,l} - q_v\right)}. \tag{6}$$

Table 2 Results of the pilot laboratory (IMT).

Date	Time	ϑ	$q_\nu(\vartheta)$	u_{et} (k=1)	u_{et} (k=1)	q_ν(23 °C)
	HH:MM	°C	mol/s	mol/s	%	mol/s
10. 10. 2012	18:41	23.80	2.640E-11	1.3E-13	0.49	2.586E-11
10. 10. 2012	18:48	23.82	2.640E-11	1.3E-13	0.49	2.585E-11
10. 10. 2012	18:59	23.85	2.643E-11	1.3E-13	0.49	2.586E-11
10. 10. 2012	19:06	23.83	2.632E-11	1.3E-13	0.49	2.576E-11
10. 10. 2012	19:14	23.88	2.649E-11	1.3E-13	0.49	2.590E-11
10. 10. 2012	19:22	23.85	2.645E-11	1.3E-13	0.49	2.587E-11
	mean	**23.84**	**2.642E-11**			**2.585E-11**
	u_{A}	**0.01**	**2.7E-14**			**2.2E-14**
11. 10. 2012	11:50	22.88	2.576E-11	1.3E-13	0.49	2.584E-11
11. 10. 2012	12:13	22.86	2.574E-11	1.3E-13	0.49	2.583E-11
11. 10. 2012	12:24	22.80	2.564E-11	1.3E-13	0.49	2.577E-11
11. 10. 2012	12:38	22.83	2.564E-11	1.3E-13	0.49	2.575E-11
11. 10. 2012	13:05	22.69	2.564E-11	1.3E-13	0.49	2.585E-11
11. 10. 2012	13:20	22.71	2.563E-11	1.3E-13	0.49	2.583E-11
	mean	**22.80**	**2.568E-11**			**2.581E-11**
	u_{A}	**0.04**	**2.5E-14**			**1.8E-14**

Room temperature was (23.5 ± 1.0) °C on the 1st day and (22.5 ± 1.0) °C on the 2nd day. Leak temperature measurement uncertainty equals 0.10 °C for $k = 1$. As one can see from Tab. 2, the temperatures of the leak varied from 22.69 °C to 23.88 °C. Hence we decided to consider also the uncertainty of the temperature correction.

Another point to consider is, whether the values obtained at the two calibration days belong to the same parent distribution. We assume that the effects contributing to the Type B uncertainties are no different at (more or less successive) calibrations days within the same sequence.

Therefore we consider the values measured on different days to be compatible, if the absolute difference between the mean values is smaller than two standard deviations of the difference:

$$\left|q_{\nu,2}-q_{\nu,1}\right| \le 2\sqrt{u_{\mathrm{A},1}^2+u_{\mathrm{A},2}^2}\,. \tag{7}$$

Herein $q_{\nu,1}$ and $q_{\nu,2}$ are the mean values determined on their respective calibration days with $u_{\mathrm{A},1}$, $u_{\mathrm{A},2}$ being their respective sample standard deviations.

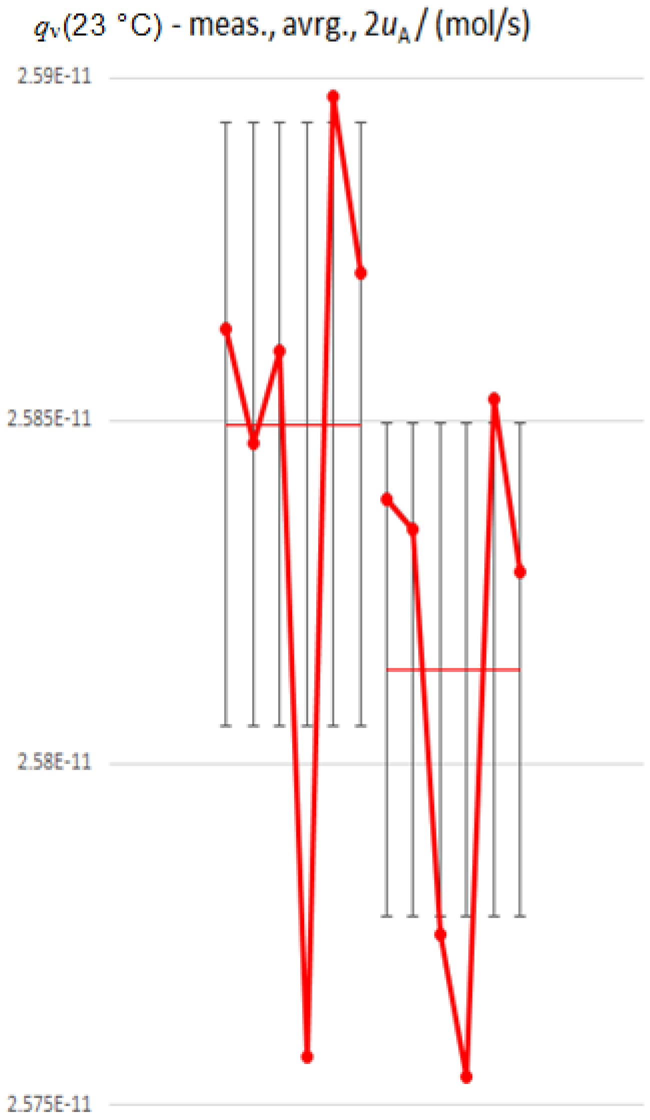

Figure 3 The results of IMT. There are shown q_{V}(23 °C), their means and twice standard deviations of these means. The time axis is out of scale, showing only ordinality and grouping into calibration days.

From Tab. 2 one can calculate that the difference of mean values on different days in a sequence ($3.6 \cdot 10^{-14}$ mol/s) agreed within two standard deviations of the difference ($5.6 \cdot 10^{-14}$ mol/s). Hence the mean and the standard deviation of the mean of all the data at the two measurement days can be taken for further evaluation.

The results of the pilot taken together are summarized in Tab. 3. In each row the mean temperature ϑ of the leak, the mean corrected leak rate q_{V}(23 °C), the temperature correction factor $tc = 1/\left(1+\alpha_T\left(T_j - 296.15\right)\right)$ and its uncertainty

$u_{tc} = \sqrt{\Delta T^2 u_\alpha^{\ 2} + \alpha^2 u_{\Delta T}^{\ 2}} \Big/ (1+\alpha\Delta T)^2$ for (k = 1), the uncertainty of the used standard u_{et} (k = 1) and Type B uncertainty calculated as $u_{\mathrm{B}} = \sqrt{tc^2 u_{\mathrm{et}}^2 + q_v^{\ 2} u_{\mathrm{tc}}^2}$ are given.

Table 3 Results of the pilot laboratory elaborated together.

ϑ	q_v (23 °C)	tc	u_{tc} (k=1)	u_{et} (k=1)	u_{B}
°C	mol/s	-	-	mol/s	mol/s
23.80	2.586E-11	0.9795	0.0025	1.3E-13	1.4E-13
23.82	2.585E-11	0.9790	0.0025	1.3E-13	1.4E-13
23.85	2.586E-11	0.9783	0.0025	1.3E-13	1.4E-13
23.83	2.576E-11	0.9788	0.0025	1.3E-13	1.4E-13
23.88	2.590E-11	0.9775	0.0025	1.3E-13	1.4E-13
23.85	2.587E-11	0.9783	0.0025	1.3E-13	1.4E-13
22.88	2.584E-11	1.0031	0.0026	1.3E-13	1.4E-13
22.86	2.583E-11	1.0037	0.0026	1.3E-13	1.4E-13
22.80	2.577E-11	1.0052	0.0026	1.3E-13	1.4E-13
22.83	2.575E-11	1.0045	0.0026	1.3E-13	1.4E-13
22.69	2.585E-11	1.0082	0.0027	1.3E-13	1.4E-13
22.71	2.583E-11	1.0076	0.0027	1.3E-13	1.4E-13

The resultant mean value of the pilot equals $2.5832 \cdot 10^{-11}$ mol/s with u_{A} calculated by (6) equal to $1.4 \cdot 10^{-14}$ mol/s and maximal u_{B} equal to $1.4 \cdot 10^{-13}$ mol/s. The combined uncertainty u (dominated by u_{B}) was calculated by

$$u = \sqrt{u_{\mathrm{A}}^2 + u_{\mathrm{B}}^2}\ . \tag{8}$$

The effective number of degrees of freedom is cca 129000, so the expanded uncertainty can be calculated using k = 2. Hence the result of the pilot is $(2.5832 \pm 0.029) \cdot 10^{-11}$ mol/s.

7. Results of CMI

7.1. Temperature coefficient of transfer standard leaks

Also CMI determined the value of the temperature coefficient of the transfer standard. It was done from the comparison data plus some extra preliminary measurements. A linear least square fit was applied to the data to determine the slope as relative temperature coefficient α_T of the flow rates:

$$\alpha_T = \frac{\Delta q_v}{q_v(23\,°\mathrm{C})\Delta T} = (2.64 \pm 0.05)\ \%/\mathrm{K}. \tag{9}$$

This value was used to correct the leak rates measured by CMI to a common temperature of 23 °C following formula (5).

7.2. Results of CMI

Table 4 Results of CMI.

Date	Time	ϑ	$q_V(\vartheta)$	u_{et} (k=1)	u_{et} (k=1)	q_V(23 °C)
	HH:MM	°C	mol/s	mol/s	%	mol/s
3.10.2012	10:28	22.89	2.615E-11	4.0E-13	1.52	2.622E-11
3.10.2012	11:37	22.94	2.624E-11	4.0E-13	1.52	2.628E-11
3.10.2012	12:14	22.90	2.573E-11	3.9E-13	1.53	2.580E-11
3.10.2012	13:03	22.97	2.560E-11	3.9E-13	1.54	2.562E-11
3.10.2012	13:50	22.99	2.623E-11	4.0E-13	1.52	2.623E-11
3.10.2012	14:41	23.04	2.637E-11	4.0E-13	1.52	2.635E-11
	mean	**22.96**	**2.605E-11**			**2.608E-11**
	st.dev.of mean	**0.03**	**1.4E-13**			**1.3E-13**
4.10.2012	12:51	22.92	2.558E-11	3.9E-13	1.54	2.563E-11
4.10.2012	13:46	22.94	2.582E-11	4.0E-13	1.53	2.587E-11
4.10.2012	14:33	22.92	2.619E-11	4.0E-13	1.52	2.624E-11
4.10.2012	15:28	22.96	2.553E-11	3.9E-13	1.54	2.555E-11
4.10.2012	16:19	22.96	2.579E-11	3.9E-13	1.53	2.582E-11
4.10.2012	17:18	22.95	2.616E-11	4.0E-13	1.52	2.620E-11
	mean	**22.94**	**2.585E-11**			**2.588E-11**
	st.dev.of mean	**0.01**	**1.3E-13**			**1.3E-13**
15.10.2012	11:45	22.89	2.543E-11	3.9E-13	1.54	2.551E-11
15.10.2012	12:40	22.88	2.633E-11	4.0E-13	1.52	2,642E-11
15.10.2012	13:27	22.93	2.580E-11	4.0E-13	1.53	2.585E-11
15.10.2012	14:12	22.99	2.584E-11	4.0E-13	1.53	2.585E-11
15.10.2012	15:15	22.95	2.546E-11	3.9E-13	1.54	2.550E-11
15.10.2012	16:12	22.92	2.545E-11	3.9E-13	1.54	2.550E-11
	mean	**22.93**	**2.572E-11**			**2.577E-11**
	st.dev.of mean	**0.02**	**1.6E-13**			**1.6E-13**
16.10.2012	9:32	23.02	2.563E-11	3.9E-13	1.54	2.562E-11
16.10.2012	10:34	23.05	2.627E-11	4.0E-13	1.52	2.623E-11
16.10.2012	11:21	22.99	2.602E-11	4.0E-13	1.52	2.603E-11
16.10.2012	12:27	23.01	2.568E-11	3.9E-13	1.53	2.568E-11
16.10.2012	13:35	22.96	2.561E-11	3.9E-13	1.54	2.563E-11
16.10.2012	14:20	22.95	2.557E-11	3.9E-13	1.54	2.560E-11
	mean	**23.00**	**2.580E-11**			**2.580E-11**
	st.dev.of mean	**0.02**	**1.3E-13**			**1.2E-13**

The results of CMI are summarized in Tab. 4. The meaning of the symbols is the same as for Tab. 3.

Room temperature was always between 22.6 °C and 23.0 °C with uncertainty 0.5 °C. Leak temperature measurement uncertainty equals 0.10 °C for k = 1. As one can see from Tab. 4, the temperatures of the leak varied from 22.88 °C to 23.05 °C. Hence we decided to consider also the uncertainty of the temperature correction.

7.3. Time-dependent behaviour of transfer standard

The physical principle of the reference leak (permeation of He from fixed reservoir) gives permanent decay of He gas flow with time. However the decay rate is usually sufficiently small so it is practically insignificant in a short period of time (two weeks), providing there is no additional loss of He from reservoir due to a leaky reservoir. Nominal decay rate at room temperature as given by the manufacturer for our transfer leak is 2 % per year. In two weeks period, which was overall duration of the comparison, the decay would be only 0.08 %, which is practically immeasurable. Linear regression of the CMI measurements that were done at the beginning and at the end of the comparison gives the decay rate of 0.07 %/d, but the R-square of the regression is only 0.12 (figure 4).

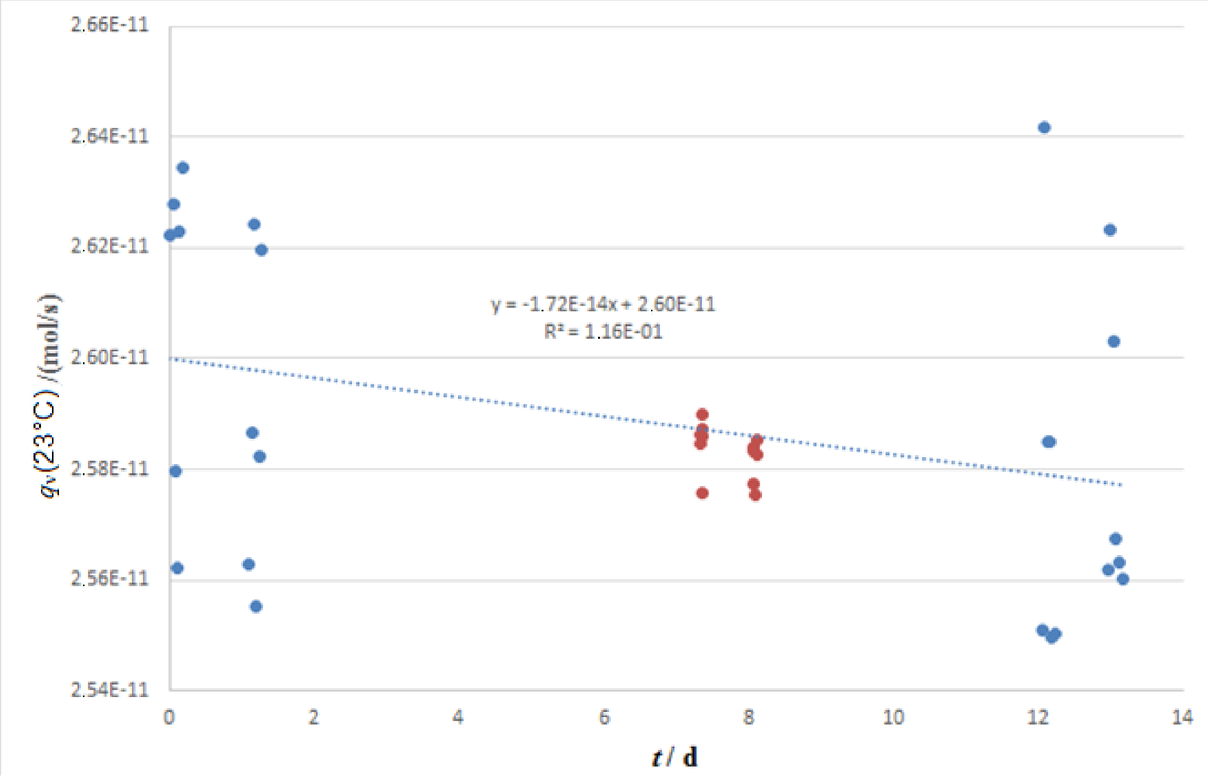

Figure 4 Time dependence of leak rate of the transfer standard.

The scatter of the measured data is significantly larger than possible drift in two weeks period, therefore we decided to use for the calculation of the equivalence of two laboratories the mean value of two CMI measurement series and neglect the drift in two weeks period. In addition the measurements of the pilot lab IMT (also shown in figure 4) were done almost in the middle of the time interval between the two measurements of CMI, so the mean value of the two measurements of CMI practically cancels out the effect of linear drift of transfer standard in present comparison.

Another point to consider is, whether the values obtained at the four calibration days belong to the same parent distribution. We assume that the effects contributing to the Type B uncertainties are no different during two weeks. Therefore we consider the values measured on different days to be compatible, if condition (7) is fulfilled.

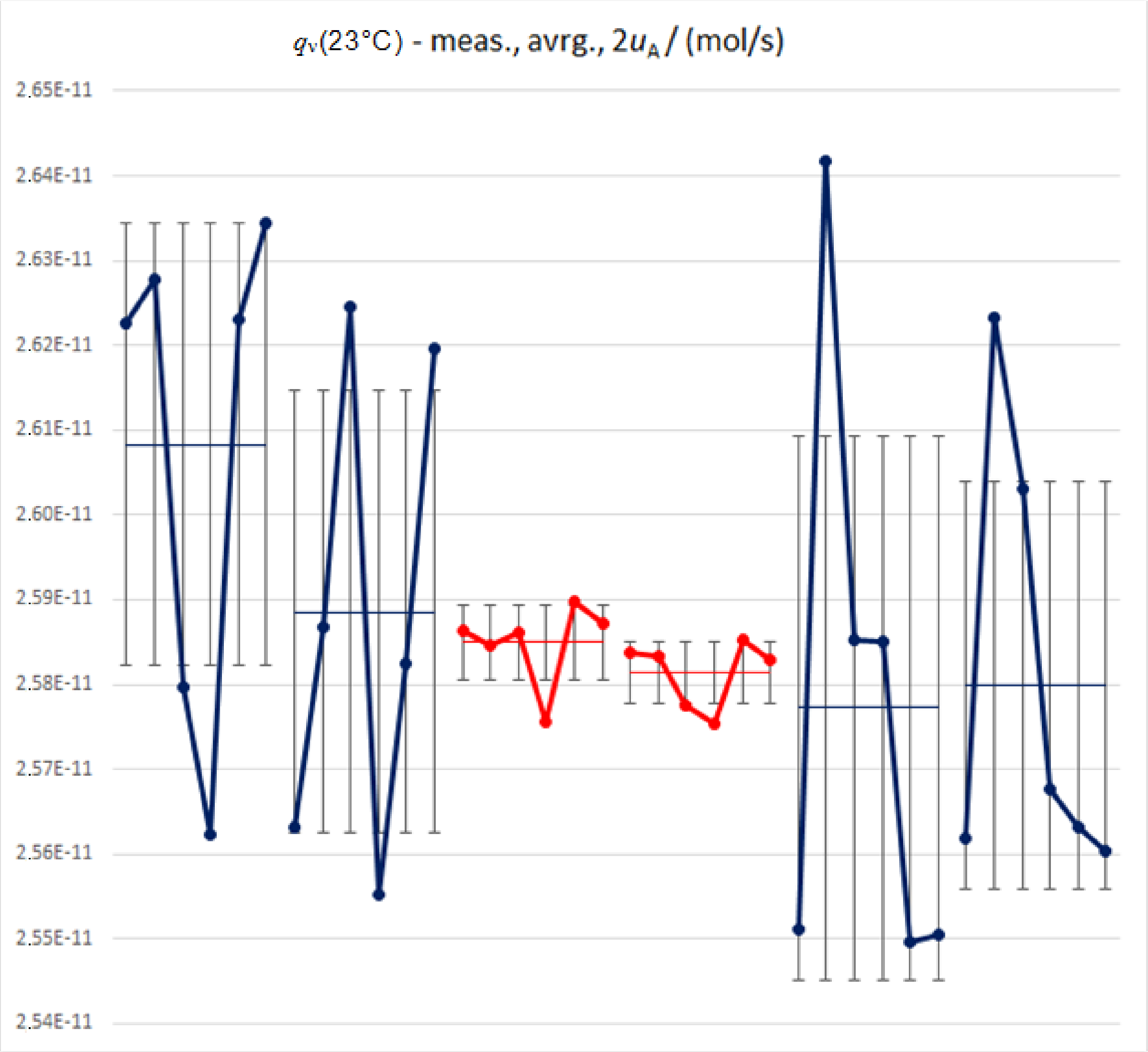

Figure 5 The results of IMT (red) and CMI (blue). There are shown q_V(23 °C), their means and double standard deviations of these means. The time axis is out of scale, showing only ordinality and grouping into calibration days.

From Tab. 4 and Fig. 5 one can see that the difference of mean values obtained on two successive days at CMI ($2.0\cdot10^{-13}$ mol/s and $2.8\cdot10^{-14}$ mol/s) agreed within two standard deviations of the differences ($3.7\cdot10^{-13}$ mol/s and $4.0\cdot10^{-13}$ mol/s).

Moreover, this is also valid for the 1st and the 3rd day, the 1st and the 4th day, the 2nd and the 3rd day and the 2nd and the 4th day, when we get the differences ($3.1\cdot10^{-13}$ mol/s, $2.8\cdot10^{-13}$ mol/s, $1.1\cdot10^{-13}$ mol/s and $8.6\cdot10^{-14}$ mol/s) agreed within double standard deviations of the differences ($4.2\cdot10^{-13}$ mol/s, $3.6\cdot10^{-13}$ mol/s, $4.1\cdot10^{-13}$ mol/s and $3.5\cdot10^{-13}$ mol/s). Hence the mean and the standard deviation of the mean of all the data at the four measurement days can be taken for further evaluation.

The results of CMI taken together are summarized in Tab. 5. In each row the mean temperature ϑ of the leak, the mean corrected leak rate q_v(23°C), the temperature correction factor $tc = 1/\left(1+\alpha_T\left(T_j - 296.15\right)\right)$ and its uncertainty for (k = 1), the uncertainty of the used standard u_{et} (k = 1) and Type B uncertainty calculated as $u_{\mathrm{B}} = \sqrt{tc^2 u_{\mathrm{et}}^2 + q_v{}^2 u_{\mathrm{tc}}^2}$ are given.

Table 5 Results of CMI elaborated together.

ϑ	u_{et} (k=1)	q_v (23 °C)	tc	u_{tc} (k=1)	u_{B}
°C	mol/s	mol/s	-	-	mol/s
22.89	4.0E-13	2.622E-11	1.0030	0.0027	4.1E-13
22.94	4.0E-13	2.628E-11	1.0015	0.0026	4.1E-13
22.90	3.9E-13	2.580E-11	1.0026	0.0027	4.0E-13
22.97	3.9E-13	2.562E-11	1.0009	0.0026	4.0E-13
22.99	4.0E-13	2.623E-11	1.0002	0.0026	4.0E-13
23.04	4.0E-13	2.635E-11	0.9989	0.0026	4.1E-13
22.92	3.9E-13	2.563E-11	1.0020	0.0027	4.0E-13
22.94	4.0E-13	2.587E-11	1.0017	0.0026	4.0E-13
22.92	4.0E-13	2.624E-11	1.0021	0.0027	4.1E-13
22.96	3.9E-13	2.555E-11	1.0010	0.0026	4.0E-13
22.96	3.9E-13	2.582E-11	1.0011	0.0026	4.0E-13
22.95	4.0E-13	2.620E-11	1.0013	0.0026	4.0E-13
22.89	3.9E-13	2.551E-11	1.0030	0.0027	4.0E-13
22.88	4.0E-13	2.642E-11	1.0033	0.0027	4.1E-13
22.93	4.0E-13	2.585E-11	1.0018	0.0026	4.0E-13
22.99	4.0E-13	2.585E-11	1.0002	0.0026	4.0E-13
22.95	3.9E-13	2.550E-11	1.0014	0.0026	4.0E-13
22.92	3.9E-13	2.550E-11	1.0020	0.0027	4.0E-13
23.02	3.9E-13	2.562E-11	0.9994	0.0026	4.0E-13
23.05	4.0E-13	2.623E-11	0.9986	0.0026	4.0E-13
22.99	4.0E-13	2.603E-11	1.0002	0.0026	4.0E-13
23.01	3.9E-13	2.568E-11	0.9998	0.0026	4.0E-13
22.96	3.9E-13	2.563E-11	1.0010	0.0026	4.0E-13
22.95	3.9E-13	2.560E-11	1.0013	0.0026	4.0E-13

The resultant mean value of the participating lab (CMI) equals 2.5884·10^{-11} mol/s with u_A calculated by (6) equal to 6.5·10^{-14} mol/s and maximal u_B equal to 4.1·10^{-13} mol/s. The combined uncertainty u (dominated by u_B) was calculated by (8).

The effective number of degrees of freedom is cca 18000, so the expanded uncertainty can be calculated using k = 2. Hence the result is (2.5884 ± 0.082)·10^{-11} mol/s.

8. Calculation of reference value and degree of equivalence

The reference value of this comparison can be calculated as

$$q_\mathrm{rv} = \frac{1}{2}\left(q_\mathrm{IMT} + q_\mathrm{CMI}\right) \tag{10}$$

and its uncertainty as

$$U_\mathrm{rv} = \frac{1}{2}\sqrt{U_\mathrm{IMT}{}^2 + U_\mathrm{CMI}{}^2}\ . \tag{11}$$

Hence $q_\mathrm{rv} =$ (2.5858 ± 0.044)·10^{-11} mol/s.

Now we can get the differences from the reference value

$$D_j = q_j - q_\mathrm{rv}\,. \tag{12}$$

Hence $D_\mathrm{IMT} =$ −2.6·10^{-14} mol/s and $D_\mathrm{CMI} =$ +2.6·10^{-14} mol/s.

The uncertainties of these differences are

$$U_{Dj} = \sqrt{U_\mathrm{rv}{}^2 + U_j{}^2}\ . \tag{13}$$

Hence U_{D_IMT} =5.2·10^{-13} mol/s

and U_{D_CMI} = 9.3·10^{-13} mol/s.

Now we can determine the degrees of equivalence

$$E_\mathrm{n} = \frac{\left|D_j\right|}{U_{Dj}}\ . \tag{14}$$

Hence $E_\mathrm{nIMT} =$ 0.05

and $E_{\mathrm{nCMI}} =$ 0.03.

9. Degree of equivalence of IMT and CMI

The pair-wise degree of equivalence of IMT and CMI can be calculated as

$$\frac{|q_{\mathrm{IMT}} - q_{\mathrm{CMI}}|}{\sqrt{U_{\mathrm{IMT}}^{2} + U_{\mathrm{CMI}}^{2}}} = 0.06. \qquad (15)$$

10. Linking to the reference value of the CCM key comparison

The reference value of K12 was $q_{\mathrm{rv\_K12}} = 4.3746 \cdot 10^{-11}$ mol/s [1]. Because a different transfer standard was used in CCM.P-K12.1, a leak rate $q_{\mathrm{rv\_K12.1}} = 2.5858 \cdot 10^{-11}$ mol/s is significantly different from $q_{\mathrm{rv\_K12}}$. Ratio of both reference values is:

$$R_{\mathrm{K12/K12.1}} = q_{\mathrm{rv\_K12}} / q_{\mathrm{rv\_K12.1}} = 1.6918. \qquad (16)$$

Difference of IMT from the reference value of the comparison CCM.P-K12 was $\Delta_{\mathrm{K12\text{-}IMT}} = -2.7 \cdot 10^{-13}$ mol/s and its associated expanded uncertainty for ($k = 2$) $U(\Delta_{\mathrm{K12\text{-}IMT}}) = 6.4 \cdot 10^{-13}$ mol/s [1].

Difference of IMT from the reference value of comparison CCM.P-K12.1 was $\Delta_{\mathrm{K12.1\text{-}IMT}} = -2.6 \cdot 10^{-14}$ mol/s and its expanded uncertainty $U(\Delta_{\mathrm{K12.1\text{-}IMT}}) = 5.2 \cdot 10^{-13}$ mol/s.

Difference of CMI from the reference value of comparison CCM.P-K12.1 was $\Delta_{\mathrm{K12.1\text{-}CMI}} = +2.6 \cdot 10^{-14}$ mol/s and its expanded uncertainty $U(\Delta_{\mathrm{K12.1\text{-}CMI}}) = 9.3 \cdot 10^{-13}$ mol/s.

In CCM.P-K12.1, IMT used the same primary system and the same measurement method as in CCM.P-K12. Relative uncertainties of IMT system at $4.37 \cdot 10^{-11}$ mol/s and at $2.58 \cdot 10^{-11}$ mol/s are the same. Relative uncertainties of CMI system are also the same at $4.37 \cdot 10^{-11}$ mol/s and at $2.58 \cdot 10^{-11}$ mol/s.

To link K12 and K12.1, the reference value $q_{\mathrm{rv\_K12.1}}$, and all associated differences and uncertainties of both labs in K12.1 have to be corrected by multiplying with $R_{\mathrm{K12/K12.1}}$.

This correction conserves the relative differences and relative uncertainties. Hence we get the following values.

$q_{\mathrm{rv\_K12.1\_C}}$ = 2.5858·10^{-11} mol/s × $R_{\mathrm{K12/K12.1}}$ = 4.3746·10^{-11} mol/s,
$U(q_{\mathrm{rv\_K12.1\_C}})$ = 4.4·10^{-13} mol/s × $R_{\mathrm{K12/K12.1}}$ = 7.4·10^{-13} mol/s,

$\Delta_{\mathrm{K12.1\text{-}IMT\_C}}$ = −2.6·10^{-14} mol/s × $R_{\mathrm{K12/K12.1}}$ = −4.4·10^{-14} mol/s,
$U(\Delta_{\mathrm{K12.1\text{-}IMT\_C}})$ = 5.2·10^{-13} mol/s × $R_{\mathrm{K12/K12.1}}$ = 8.8·10^{-13} mol/s,

$\Delta_{\mathrm{K12.1\text{-}CMI\_C}}$ = 2.6·10^{-14} mol/s × $R_{\mathrm{K12/K12.1}}$ = 4.4·10^{-14} mol/s,
$U(\Delta_{\mathrm{K12.1\text{-}CMI\_C}})$ = 9.3·10^{-13} mol/s × $R_{\mathrm{K12/K12.1}}$ = 1.57·10^{-12} mol/s.

Now the link to CCM.P-K12 can be determined. Difference of the CMI from the reference value of CCM.P-K12 is:

$$\Delta_{\mathrm{K12\text{-}CMI}} = \Delta_{\mathrm{K12\text{-}IMT}} - \Delta_{\mathrm{K12.1\text{-}IMT\_C}} + \Delta_{\mathrm{K12.1\text{-}CMI\_C}} = \tag{17}$$
$$= (-2.7\cdot10^{-13} + 4.4\cdot10^{-14} + 4.4\cdot10^{-14})\ \mathrm{mol/s} = -1.8\cdot10^{-13}\ \mathrm{mol/s}.$$

Uncertainty of the difference of CMI from the reference value of CCM.P-K12 is:
$U(\Delta_{\mathrm{K12\text{-}CMI}}) = U(\Delta_{\mathrm{K12.1\text{-}CMI\_C}})$ = 1.57·10^{-12} mol/s.

And finaly the equivalence of CMI to the CCM.P-K12 reference value is:
$\varepsilon_{\mathrm{X}} = \left|\Delta_{\mathrm{K12\text{-}CMI}}\right| / U\left(\Delta_{\mathrm{K12\text{-}CMI}}\right)$ = 0.12.

It can be easily seen that CMI is also equivalent with the reference value of key comparison CCM.P-K12.

11. Discussion and conclusions

CMI proved equivalence both with IMT and with the reference value of the key comparison CCM.P-K12.

12. References

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