Final report on key Comparison SIM-Euromet.M.P-BK3 (bilateral comparison) in the pressure range from $3 \cdot 10^{-4}$ Pa to 0.9 Pa

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Content

1. Introduction

In the frame of a technical cooperation between the Federal Ministry for Economic Cooperation and Development of Germany and the National Council of Science and Technology (CONACYT) of Mexico a vacuum primary standard was built at the Centro Nacional de Metrologia (CENAM), the National Metrology Institute of Mexico. The vacuum section of the Physikalisch-Technische Bundesanstalt (PTB), the National Metrology Institute of Germany, helped CENAM to create this primary standard. It is based on the static expansion method and is described in Section 2.

As a conclusion of this cooperation in 2002 it was decided by the related working group for low and very low pressures of the Comité Consultatif de la masse et les grandeurs apparentéès (CCM) to perform a bilateral comparison between CENAM and PTB according to the guidelines of the BIPM [1]. This comparison was later listed as key comparison as SIM-Euromet.M.P-BK3 in the BIPM data base.

The key comparison SIM-Euromet.M.P-BK3 was directly connected to and following the RMO comparison Euromet.M.P-K1.b. The same transfer standards were used and the same calibration procedure adopted in the two comparisons. The Laboratory for Vacuum Metrology at PTB acted as the pilot laboratory in both comparisons. In consideration of the accuracy of the available transfer standards, the pressure range was specified to $3 \cdot 10^{-4}$ Pa ... 0.9 Pa.

The objective of the comparison was to determine the degree of equivalence of absolute pressure standards between PTB and CENAM, and indirectly between EUROMET, a cooperative voluntary organisation between the national metrology institutes in Europe, and SIM, a similar organisation in America. In addition to the measurand, the crucial value for the determination of the degree of equivalence is the uncertainty of the generated pressure in the calibration standard. This value was considered as solely the responsibility of the participating labs and had to be reported as part of the calibration report. In contrast, all additional uncertainties that were related to the transfer standard were evaluated by the pilot laboratory in order to have a uniform uncertainty analysis for all participants and in order to emphasise the importance of the reported uncertainty of the generated pressure.

Since PTB took part in key comparisons organised by CCM in overlapping pressure ranges, the comparison also allows the possibility of finding deviations from the CCM reference value for CENAM for a part of the pressure range under consideration.

Two spinning rotor gauges were chosen as transfer standards, which were to be calibrated at the following target pressures: $3{\cdot}10^{-4}$ Pa, $9{\cdot}10^{-4}$ Pa, $3{\cdot}10^{-3}$ Pa, $9{\cdot}10^{-3}$ Pa, $3{\cdot}10^{-2}$ Pa, $9{\cdot}10^{-2}$ Pa, 0.3 Pa, and 0.9 Pa.

2. Participating laboratories and their standards

Table 1 lists the two participating laboratories and characteristics of their standards.

Table 1 List of participants in alphabetic order and the standards used for the calibration of the transfer standards.

Laboratory	Standard	Character of standard	Traceable to:	CMC listed
Centro Nacional de Metrologia (CENAM) Mexico	Static expansion system	Primary	independent	no
Physikalisch-Technische Bundesanstalt (PTB) Germany	Static expansion system	Primary	independent	yes

The CENAM's pressure standard (SEE-1) is based on the static expansion method (also called serial expansion method). The SEE-1 system is used to measure medium and high vacuum within the range of $1{\cdot}10^{-5}$ Pa to $1{\cdot}10^{3}$ Pa absolute pressure. It consists of four known volumes, two small volumes of nominally 0.5 L and 1 L and two expansion chambers, 50 L and 100 L nominally. With this primary standard the Boyle–Mariotte law is applied: A known small volume of gas at a known relatively high pressure is expanded into a previously evacuated, larger volume (under isothermal conditions). This generates a pressure drop which depends on the initial and final volumes' ratio.

Also the primary standard of the PTB is a static expansion system, called SE1, in which pressures are generated by expanding gas of known pressure from a very small volume V_4 of 17 mL directly into a volume of 233 L, or by two successive expansions from a volume V_1 = 17 mL into a intermediate volume of 21 L including V_4 and then from V_4 into the 233 L vessel. The regular operational range of SE1 is 10^{-6} Pa up to 1 Pa. Due to the relatively high volume ratios, the initial pressure must be reduced below 1 kPa in the calibration sequence of this comparison, when for $9{\cdot}10^{-3}$ Pa one expansion instead of two at lower pressures is performed. For this reason the uncertainty of the initial pressure measurement is higher and contributes significantly in an intermediate pressure regime (see Section 7). The system is described in more detail in references [2] and [3].

3. Transfer standards

Two spinning rotor gauges (SRG) have been chosen as transfer standard for the comparison. The SRG [4] is widely accepted as a transfer standard [5] due to its measurement accuracy and long-term and transport stability [6], [7]. Two devices were used in order to further reduce the influence of transport-instabilities, to produce redundancy, and to increase the accuracy of the comparison.

Each laboratory used its own controllers to operate the two spinning rotor gauges. To date there is no published evidence to indicate that a different controller and gauge head would have an influence on the calibration results (concerning the accommodation coefficient) of a rotor/finger combination.

PTB prepared and pre-tested the two spinning rotor gauges (Table 2). Rotor 1 was an etched stainless steel ball, with a nominal diameter of 4.762 mm, embedded in a 8 mm OD 8 tube ("finger") with a DN16 CF flange, numbered 25UM. Rotor 2 was an INVAR ball, with a nominal diameter of 4.50 mm, located in a similar finger, numbered 23UM.

Each finger was sealed with a special all metal valve [6] which had two functions: 1. To seal the rotor in the finger so that it could be transported under vacuum. 2. To fix the rotor during transportation so that the surface would not be changed due to milling and friction effects of the rolling ball.

Transport under vacuum required that the valve was only opened when it was connected to high vacuum and, before transportation, the valve was closed under high vacuum conditions. To ensure free spinning of the rotor the valve had to be completely opened.

Table 2 Transfer standards used for the comparison

Transfer standard	**Rotor 1**	**Rotor 2**
Material	Etched stainless steel	Invar
Nominal diameter	4.762 mm	4.5 mm
Nominal density	$7.715 \cdot 10^3$ kg/m^3	$8.2 \cdot 10^3$ kg/m^3

Data exists from 1994 onwards for calibration of each rotor at PTB. Both rotors showed a very good long-term stability of their effective accommodation coefficient with the relative difference of the calibration constant not larger than 0.9% between the smallest and the largest value. Typical long-term instabilities per year were 0.2% for rotor 1 and 0.1% for rotor 2.

4. Calibration constant

The value to be calibrated by each laboratory j for each pressure for each rotor i was the effective accommodation coefficient σ_{ij} [4], often called σ_{eff}, which is mainly determined by the tangential momentum accommodation coefficient of the gas molecules to the rotor, and partly by the energy accommodation factor [4] and additionally by using nominal values for diameter and density of the rotors instead of the real ones.

σ_{ij} was determined by the following equation:

$$\sigma_{ij} = \sqrt{\frac{8kT_j}{\pi m}} \cdot \frac{\pi d_i \rho_i}{20 p_{stj}} \left(\left(\frac{\dot{\omega}}{\omega} \right)_i - RD_i(\omega) \right) \tag{1}$$

Herein p_{stj} is the generated pressure in the standard, T_j the temperature of gas in the calibration chamber, d_i and ρ_i are the (nominal) diameter and density of the rotor i, m is the molecular mass of nitrogen, ($\dot{\omega}/\omega$), also called DCR, is the relative deceleration rate of the rotor frequency ω, and RD is a pressure independent residual drag, caused by eddy current losses in the surrounding metal structures and the rotor itself.

RD is generally a function of ω, $RD(\omega)$, so that it was required that, whenever σ_{ij} was determined, the value of ω also had to be measured in order to subtract the correct $RD(\omega)$ in Eq. (1). For measuring $RD(\omega)$ three options were offered by the comparison protocol.

Option 1: Before starting the calibrations the rotor frequency dependence of the residual drag (in unit DCR = s^{-1}) could be measured over a long period of time. The rotor frequency had to cover the full range that may occur during a calibration, that is normally $\omega/2\pi$ = 405 s^{-1} ... 415 s^{-1}, which may take 48 h. For this, the residual pressure in the standard must be below 10^{-6} Pa.

Option 2: It is possible to shorten the above measurement of the residual drag (offset) by intentionally letting gas into the vacuum system. After re-acceleration of the rotor to 415 s^{-1}, it was suggested to introduce 0.1 Pa of nitrogen gas and wait until the frequency drops to 412 s^{-1}, pump down to residual pressure and re-measure the offset. This procedure should be repeated for 409 s^{-1}, 406 s^{-1}, and 415 s^{-1} again to check the stability of the offset at one frequency. The whole sequence could be repeated several times to reduce the scatter of $RD(\omega)$.

Option 3: $RD(\omega)$ could be determined during the course of the calibrations by pumping down the vacuum system to residual pressure conditions after each target pressure point.

In all cases a linear least square fit had to be applied to obtain the function $RD(\omega)$.

Option 3 was the preferred option, since Options 1 and 2 require a high temperature stability of the laboratory over a long period of time due to the dependence of RD on temperature drifts. Option 3 was also recommended to check the data obtained by Options 1 or 2.

The determination of $RD(\omega)$ was considered as part of the calibration, because it affects its accuracy, and was the responsibility of each laboratory.

It is well known [4] that in the molecular regime up to about $3 \cdot 10^{-2}$ Pa σ_{eff} is pressure independent. For this reason, it was clear, a priori, that any pressure dependencies are likely to be due to measurement errors or problems of the calibration standard.

In the protocol, no specific temperature for the calibration was requested. It was found [8] that σ_{eff} may be slightly dependent on the temperature of the rotor. For this reason we introduced an additional uncertainty for the pressures deduced from σ_{eff}, since calibrations were performed at different temperatures (CENAM around 294.4 K, PTB close to 296.4 K).

5. Organisation of the comparison and chronology

In order to reduce the effects of transport instabilities of the rotors, it was decided that the rotors were hand carried from and to the pilot laboratory and that the pilot lab would perform calibrations before and after transport to CENAM. For the determination of the transport instability it was assumed that the primary standard of the pilot laboratory is stable. To substantiate this assumption the pilot lab used a third SRG (check standard), which was calibrated at the same time as the transfer gauges.

Table 3 presents the actual chronology of the calibrations. The two PTB calibrations have been named PTB 6 and PTB 7, because they followed PTB 1 to PTB 5, which were carried out between April 2000 and February 2002 in the frame of the comparison Euromet.M.P-K1.b.

Table 3 Chronology of measurements

Calibrating Laboratory	Date	Note
PTB 6	April, 18 and 22, 2002	After this, hand carried to CENAM
CENAM, Mexico	May, 9 and 14, 2002	After this, hand carried to PTB
PTB 7	June, 25 and 26, 2002	Comparison finished

6. Calibration procedure and results to be reported

The following calibration procedure was agreed upon before the comparison: Each laboratory was to calibrate the two SRGs at the following 8 nominal target pressures p_t for nitrogen pressure in ascending order: $3\cdot10^{-4}$ Pa, $9\cdot10^{-4}$ Pa, $3\cdot10^{-3}$ Pa, $9\cdot10^{-3}$ Pa, $3\cdot10^{-2}$ Pa, $9\cdot10^{-2}$ Pa, 0.3 Pa, 0.9 Pa.

A tolerance of ± 10% in hitting the nominal pressure was accepted for $p_t < 9\cdot10^{-2}$ Pa and ± 5% for $9\cdot10^{-2}$ Pa, 0.3 Pa, 0.9 Pa. Each target pressure had to be generated 3 times. This meant that after a measurement at the target point, the system was pumped down to residual pressure conditions and the same point re-generated. In total 8·3 = 24 points were measured in this way and were considered as one calibration sequence. It was required that this calibration sequence be repeated at least once on another day.

The readings of each of the SRGs were to be sampled in the following manner:

- 10 repeat points at 30 s intervals for the target points $3\cdot10^{-4}$ Pa, $9\cdot10^{-4}$ Pa, and $3\cdot10^{-3}$ Pa.
- 5 repeat points at 30 s intervals for $9\cdot10^{-3}$ Pa, $3\cdot10^{-2}$ Pa, $9\cdot10^{-2}$ Pa.
- 5 repeat points at 30 s intervals for 0.3 Pa and 0.9 Pa.

Regardless of the option chosen for offset determination, it was required that the offset be measured during the calibration:

- At the beginning of the calibration sequence.
- After the target pressures $3\cdot10^{-4}$ Pa, $9\cdot10^{-4}$ Pa, $3\cdot10^{-3}$ Pa, and 0.9 Pa (end of calibration sequence).

This was done in order to realise option 3 or to check the data obtained with option 1 or 2.

For three reasons it was agreed that no bake-out should be performed with the rotors:

1) Bake-out is a time consuming factor and would make it impossible to have a period of one month for each laboratory.
2) σ_{eff} may change after a bake-out.
3) The rotors were transported under vacuum, so that there was no real need for a bake-out of the rotors.

Since σ_{eff} is pressure dependent for $p > 3\cdot10^{-2}$ Pa, which may make the comparison inaccurate, when the target pressures are not hit exactly, it was agreed that a linear fit line through the points $\sigma_{ij}(p_{stj} \approx 9\cdot10^{-2}$ Pa), $\sigma_{ij}(p_{stj} \approx 0.3$ Pa), and $\sigma_{ij}(p_{stj} \approx 0.9$ Pa) would be used to calculate σ_{ij} at the exact target pressures in the following manner:

$$\sigma_{ij} = (\sigma_{ij})_{\text{det}} + (p_t - p_{stj}) \cdot m_i \quad . \tag{2}$$

p_t are the nominal target pressures 0.09 Pa, 0.3 Pa, 0.9 Pa, p_{stj} the generated pressures close to p_t, $(\sigma_{ij})_{\text{det}}$ the values determined by the calibration at p_{stj}, and m_i the slope of the fit line for rotor i.

At the end of this calibration procedure, for each generated p_{stj} near the respective target point and for each rotor i and for each of the calibration sequences a value for σ_{ij} existed and was reported to the pilot laboratory. With the value of σ_{ij} each laboratory reported the standard uncertainty $u(p_{stj})$ of p_{stj}.

Both CENAM and PTB used option 3 to determine the offset.

7. Uncertainties of primary standards

Table 4 presents the relative standard uncertainties due to Type B uncertainties for the two primary standards. Type A uncertainties will show up in the scatter of data at repeat measurements, so that it was sufficient to report the Type B uncertainties only.

Table 4 Relative standard uncertainties of generated pressures due to systematic effects (Type B) as reported by the participants.

p_t in Pa	CENAM	PTB
3.00E-04	2.66E-03	2.42E-03
9.00E-04	2.64E-03	2.42E-03
3.00E-03	2.12E-03	2.42E-03
9.00E-03	2.11E-03	3.15E-03
3.00E-02	2.11E-03	3.15E-03
9.00E-02	2.11E-03	3.04E-03
3.00E-01	1.67E-03	1.67E-03
9.00E-01	1.67E-03	1.67E-03

8. Uncertainty of reported measured values

The model of the reported value, σ_{ij}, has been formulated in Eq. (1). If we introduce,

$$K_i = \sqrt{\frac{8k \cdot 296.15\,\text{K}}{\pi m}} \cdot \frac{\pi d_i \rho_i}{20} \,, \tag{3}$$

and

$$DCR_i \equiv \left(\frac{\dot{\omega}}{\omega}\right)_i , \tag{4}$$

and consider that the effective accommodation coefficient has been measured n =6 times, σ_{ijk}, k=1...n, then we can write,

$$\sigma_{ijk} = \sqrt{\frac{T_{jk}}{296.15}} \cdot \frac{K_i}{p_{stjk}} \left(DCR_{ik} - RD_{ik}(\omega)\right) \tag{5}$$

and we will replace Eq. (1) by taking the mean of the repeated measurements to give

$$\sigma_{ij} = \frac{1}{n} \sum_{k=1}^{n} \sigma_{ijk} . \tag{6}$$

The same values for *k, m,* d_i, *and* ρ_i were used by each laboratory and the K_i were therefore fully correlated, so that in effect no uncertainty needed to be attributed to K_i (A systematic error in d_i, for example, would be calibrated into σ_{ij} in the same way in each laboratory and would not affect the result of the comparison). All type A uncertainties of values on the right hand side of Eq. (5) will contribute to the scatter of σ_{ijk} and so to the standard deviation of σ_{ij}. Therefore, since Type A uncertainties are accounted for by the standard deviation, for calculation of the overall uncertainty of σ_{ij} only the Type B uncertainties of values on the right hand side of Eq. (5) have to be evaluated for inclusion. For DCR_i there is no such uncertainty. $RD(\omega)$ is not determined at the same time as DCR_i, but before or after the measurement, and therefore has a Type B uncertainty. Also the gas temperature and the generated pressure p_{stj} will have Type B uncertainties, which are known before the measurements.

For this reason the variance in σ_{ij} is given by:

$$u_{\sigma_{ij}}{}^2 = \frac{n-1}{n-3} s_{\sigma_{ij}}^2 + \left(\frac{\partial \sigma_{ij}}{\partial RD_i}\right)^2 u_{RD_i}{}^2 + \left(\frac{\partial \sigma_{ij}}{\partial T_j}\right)^2 u_{T_j}{}^2 + \left(\frac{\partial \sigma_{ij}}{\partial p_{stj}}\right)^2 u_{p_{stj}}{}^2 , \tag{7}$$

where $s_{\sigma_{ij}}^2$ is the square of the standard deviation of the mean of the repeat measurements σ_{ijk} and where we understand that all standard uncertainties u are due to systematic effects which do not contribute to the scatter of σ_{ij} . Since only 6 measurements were taken with an effective degree of freedom of 5, $s_{\sigma_{ij}}$ was multiplied by $\sqrt{(n-1)/(n-3)}$, i.e. 1.29, as suggested by Kacker and Jones [9]. The last term in Eq. (7) is due the generated pressure as discussed in Section 7, all the other terms are due to uncertainties of the measurement (transfer) standard.

The sensitivity coefficients are:

$$\left(\frac{\partial\sigma_{ij}}{\partial RD_i}\right)=-\frac{K_i}{p_{stj}}\cdot\sqrt{\frac{T_j}{296.15}} \tag{8}$$

$$\left(\frac{\partial\sigma_{ij}}{\partial p_{stj}}\right)=-\frac{K_i}{p_{stj}^2}\cdot\sqrt{\frac{T_j}{296.15}}\left(DCR_i-RD_i\right) \tag{9}$$

$$\left(\frac{\partial\sigma_{ij}}{\partial T_j}\right)=\frac{1}{2}\frac{K_i}{p_{stj}}\frac{1}{\sqrt{296.15}}\frac{1}{\sqrt{T_j}}\left(DCR_i-RD_i\right) \tag{10}$$

$u(p_{stj})$ and $u(T_j)$ were reported by each laboratory, where it is assumed that $T_{jk} \approx T_j$ (constant temperature of standard during 3 repeat measurements). The following effects may contribute to the uncertainty of the residual drag RD_i :

- the scatter of the measurement results,
- the imprecisely known frequency dependence of the offset,
- a possible short term drift of the offset value between its determination and the time of calibration
- a possible long term drift of the offset value between its determination and the time of calibration.

The latter effect was excluded by the fact that both laboratories used Option 3 to determine RD_i. There were no significant shifts (more than the scatter of the data) of the offset in the time frame for Option 3. The uncertainty due to the first three effects was considered by the evaluation of data in the pilot laboratory in the following manner: A linear fit line through all measured $RD_i(\omega)$ was calculated (least squares). The 95% confidence limits of the predicted values were calculated. The difference between the upper and the lower confidence limit was nearly independent of ω in the measurement range. For standard uncertainty $u(RD_i(\omega))$, ¼ of the difference between the upper and the lower confidence limit was taken. With this procedure, both the scatter of $RD_i(\omega)$, the uncertainty of the frequency dependence, and possible short term shifts (within about 60 min) were included.

9. Reported results of the laboratories

Since each laboratory carried out 2 calibration sequences it was possible to check if significant changes could be observed between the σ_{ij} for the different sequences. Such a change could be important for the comparison for two reasons:

1) If an instability in the calibration constant of a transfer standard occurred during the calibrations in a single laboratory, it could be taken into account by normalisation. If only one SRG showed a change in value it is highly probable that such an instability was detected.

2) If the primary standard showed an instability, it is highly probable that both σ_{1j} and σ_{2j} would show a shift of same size in the same direction. This could help the participant to improve their standard.

Fortunately, no such changes of the calibration constant of the transfer standards were found during the 3 pairs of calibration sequences.

Therefore the mean value of all data for a single rotor and single target pressure could be taken for data reduction:

$$\sigma_{ij} = \frac{1}{n}\sum_{k=1}^{n}\sigma_{ijk} \quad n = 6 \qquad \text{Eq. (6)}$$

The results reported by each laboratory and the corresponding uncertainties according to Eq. (7) are shown in the following tables and figures.

Table 5 The mean values σ_{1j} of the reported results for Rotor 1 and the uncertainties as calculated from Eq. (7).

p_t/Pa	PTB6		CENAM		PTB7	
	σ_1	$u(\sigma_1)$	σ_1	$u(\sigma_1)$	σ_1	$u(\sigma_1)$
3.00E-04	1.1478	0.0278	1.1438	0.0201	1.1506	0.0101
9.00E-04	1.1490	0.0091	1.1456	0.0073	1.1487	0.0043
3.00E-03	1.1495	0.0040	1.1458	0.0031	1.1490	0.0029
9.00E-03	1.1496	0.0037	1.1460	0.0025	1.1514	0.0037
3.00E-02	1.1507	0.0036	1.1459	0.0025	1.1510	0.0037
9.00E-02	1.1489	0.0035	1.1454	0.0025	1.1485	0.0035
3.00E-01	1.1432	0.0019	1.1406	0.0020	1.1426	0.0019
9.00E-01	1.1274	0.0019	1.1255	0.0013	1.1266	0.0019

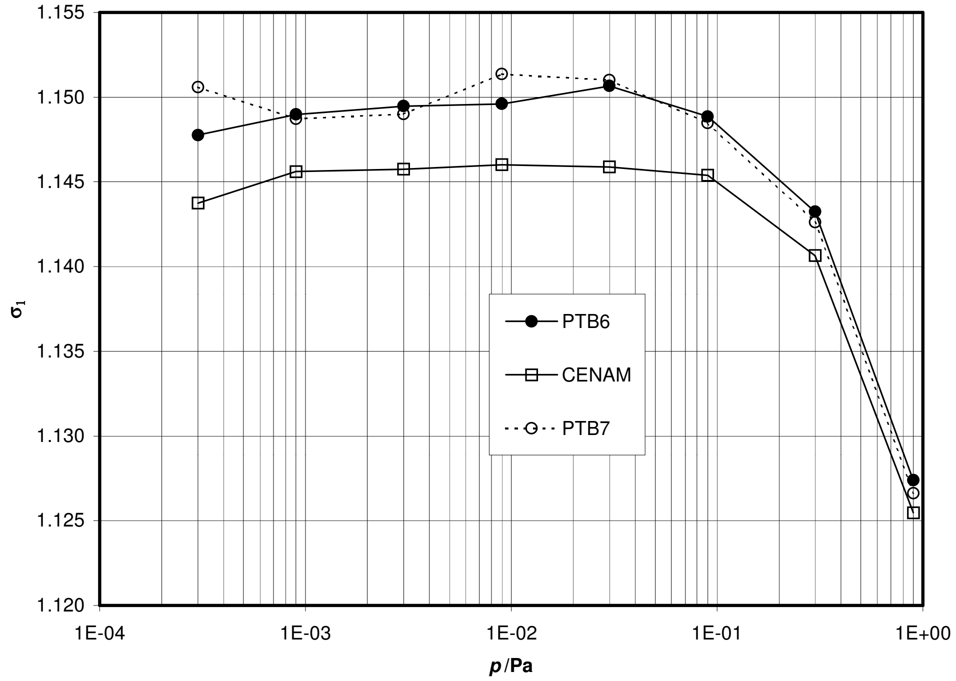

Figure 1 Graphical presentation of the results of Rotor 1 (Table 5). Uncertainties are not shown for better visibility and can be taken from Table 5.

Table 6 The mean values σ_{2j} of the reported results for Rotor 2 and the uncertainties as calculated from Eq. (7).

p_t/Pa	PTB6		CENAM		PTB7	
	σ_2	$u(\sigma_2)$	σ_2	$u(\sigma_2)$	σ_2	$u(\sigma_2)$
3.00E-04	1.1150	0.0035	1.1120	0.0055	1.1160	0.0050
9.00E-04	1.1147	0.0028	1.1119	0.0034	1.1147	0.0030
3.00E-03	1.1148	0.0027	1.1117	0.0024	1.1148	0.0027
9.00E-03	1.1156	0.0035	1.1117	0.0024	1.1177	0.0036
3.00E-02	1.1167	0.0035	1.1113	0.0024	1.1174	0.0035
9.00E-02	1.1150	0.0034	1.1110	0.0024	1.1149	0.0034
3.00E-01	1.1098	0.0019	1.1067	0.0019	1.1095	0.0019
9.00E-01	1.0956	0.0018	1.0930	0.0013	1.0951	0.0018

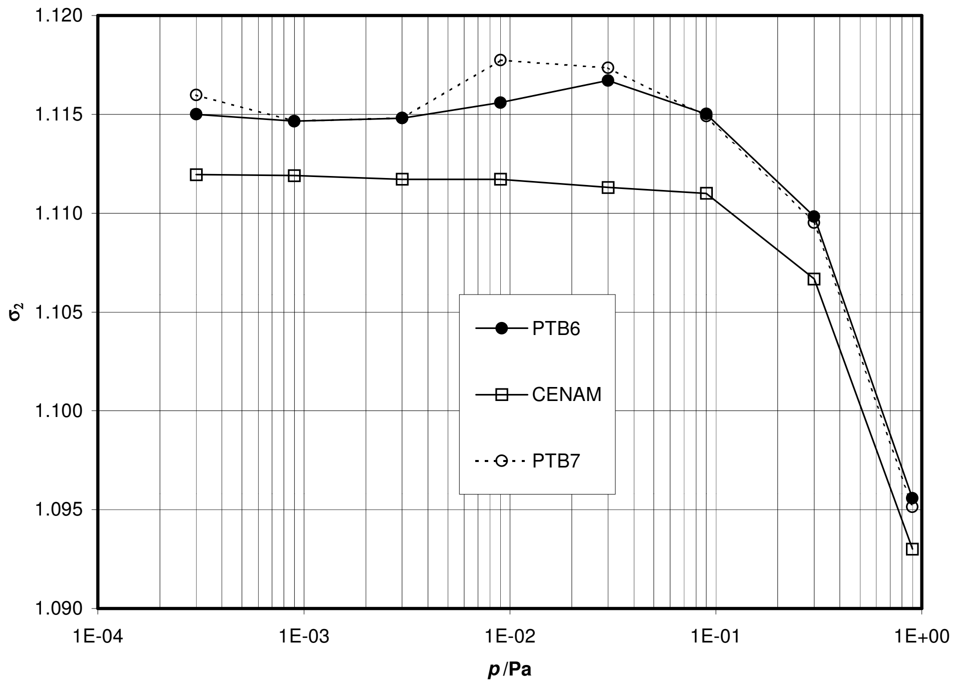

Figure 2 Graphical presentation of the results of Rotor 2 (Table 6). Uncertainties are not shown for better visibility and can be taken from Table 6.

From these results it can be seen that the CENAM values for both rotors are systematically lower than the values obtained at PTB.

Especially for PTB7 an upwards shift of the values between $3{\cdot}10^{-2}$ Pa and $9{\cdot}10^{-2}$ Pa can be noticed. Since it is known that σ is independent in the molecular regime, this shift indicates a problem in the PTB standard, probably related to the measurement of the initial pressure (see Section 2). The value of the shift, however, is within the stated uncertainties (Section 7).

It can also be observed that the values before transport to (PTB6) and after transport from CENAM (PTB7) were almost identical, which indicates a good transport stability.

10. Stability of transfer gauges

In order to monitor the transport stability of the calibration constant of the two rotors during the course of the comparison, the mean values of σ_1 and σ_2 between $9{\cdot}10^{-4}$ Pa and $3{\cdot}10^{-2}$ Pa of the pilot lab were calculated. Table 7 shows the result. Rotor 3 was the check standard that did not travel.

Table 7 The mean values of σ_1 and σ_2 between $9\cdot10^{-4}$ Pa and $3\cdot10^{-2}$ Pa for the two PTB calibrations and the respective scatter (standard deviation s) of the mean. Rotor 3 with the value σ_3 did not travel and served as check standard for PTB.

	σ_1	$s(\sigma_1)$	σ_2	$s(\sigma_2)$	σ_3	$s(\sigma_3)$
PTB6	1.1497	0.0004	1.1154	0.0005	1.1578	0.0003
PTB7	1.1500	0.0007	1.1161	0.0008	1.1589	0.0009

To compare primary standards it would be ideal to calibrate the transfer standards at the same time on the different primary standards. Since this is not possible, we will assume that the mean value of the two pilot lab calibrations (at the beginning and at the end of the transportation to and from CENAM) is the best approximation of coincident time to compare with the participants' values in the loop. Since the measured changes between PTB6 and PTB7 are within the standard deviation of each mean value, it is reasonable to assume that both effective accommodation coefficients did not change during this bilateral comparison. It is highly improbable that a possible shift in σ at the CENAM site would be exactly cancelled for both SRGs after the return transport to PTB. This was different during the previous Euromet comparison carried out with the same transfer standards, where normally at least one of the SRG shifted during a transportation loop.

11. Data reduction and evaluation of the degree of equivalence

As outlined in the last section, the most reasonable assumption is that the transport instability of the two SRGs were zero during this comparison. For this reason all values taken at the pilot lab PTB can be assumed to belong to the same parent population and the mean of all these data is taken:

$$\sigma_{ij} = \frac{1}{n}\sum_{k=1}^{n}\sigma_{ijk} \quad n = 12 \ . \tag{11}$$

Since one of the goals of this comparison is to compare the generated pressures of the two standards, a pressure value has to be generated from the σ_{ij}. For each laboratory and for each SRG i a value of indicated pressure p_{ij} for a common hypothetical target pressure p_t can be calculated with the following equation:

$$p_{ij} = p_t \cdot \sigma_{ij} \quad i = 1,2 \quad j = 1,2 \tag{12}$$

σ_{ij} denotes the mean accommodation coefficient according to Eq. (6) of SRG i as determined by CENAM (j=1) or according to Eq. (11) of SRG i as determined by PTB (j=2).

The method adopted here is to use the σ_{ij} to predict gauge readings that would be observed, when the different standards are set to generate pressures of the same value and at coincident time. The difference in the predicted gauge readings is taken as an indicator of the difference between true pressures actually realised by the different standards ("generated pressures") when the two laboratories state the same calculated value. This latter difference between calculated pressures, when the standards are set to produce exactly the same transfer gauge reading near the target pressure, is to a very good approximation (provided that the differences are small) equal to the difference in the predicted gauge readings but of opposite sign.

As was briefly mentioned at the end of Section 4 it was found by Jousten [8] that σ_{ij} may be slightly temperature dependent. The size of this effect varies from rotor to rotor and in addition is dependent on the specific surface condition of a single rotor. Relative temperature changes of $(\Delta\sigma_{eff}/\Delta T)/\sigma_{eff} = -1\cdot 10^{-4}\,/\,\mathrm{K}$ to $-4\cdot 10^{-4}\,/\,\mathrm{K}$ were found around room temperature. The mean temperatures during calibrations at CENAM (294.4 K) and PTB (296.4 K) differed by 2 K. Since the temperature dependence of σ_{eff} of the two transfer standards was not measured and also may have changed during the comparison, the only possibility to consider this effect is to add an uncertainty for the p_{ij} in Eq. (12). We assumed a mean calibration temperature of 295.4 K, so that each laboratory differed by 1 K from this temperature, and a possible temperature dependence of $(\Delta\sigma_{eff}/\Delta T)/\sigma_{eff} = -2\cdot 10^{-4}\,/\,\mathrm{K}$ to calculate the standard uncertainty of the temperature effect for the p_{ij} in Eq. (12):

$$u_{T\sigma}(p_{ij}) = 2\cdot 10^{-4}\, p_{ij}\,. \qquad (13)$$

It should be emphasised that this uncertainty contribution is only due to an incomplete specification of the protocol. This uncertainty, however, is small compared to the standard uncertainties of the generated pressures (see Table 4).

Since p_t is simply a numerical value without uncertainty, the uncertainty of p_{ij} is calculated from the following equation:

$$u(p_{ij}) = p_{ij}\sqrt{\left(\frac{u(\sigma_{ij})}{\sigma_{ij}}\right)^2 + \left(\frac{u_{T\sigma}(p_{ij})}{p_{ij}}\right)^2} \qquad (14)$$

$u(\sigma_{ij})$ was given in Eq. (7), and $u_{T\sigma}(p_{ij})$ in Eq. (13).

The following tables show the results for the p_{ij} obtained from Eqs. (12) and (14).

Table 8 The predicted gauge readings and their uncertainties as obtained from Eqs. (12) and (14) for rotor 1.

p_t in Pa	p_{1PTB} in Pa	$u(p_{1PTB})$	p_{1CENAM} in Pa	$u(p_{1CENAM})$
3.0E-04	3.448E-04	7.9E-06	3.431E-04	6.0E-06
9.0E-04	1.034E-03	8.2E-06	1.031E-03	6.6E-06
3.0E-03	3.448E-03	1.2E-05	3.437E-03	9.4E-06
9.0E-03	1.035E-02	3.4E-05	1.031E-02	2.3E-05
3.0E-02	3.453E-02	1.1E-04	3.438E-02	7.5E-05
9.0E-02	1.034E-01	3.1E-04	1.031E-01	2.3E-04
3.0E-01	3.429E-01	5.8E-04	3.422E-01	5.9E-04
9.0E-01	1.014E+00	1.7E-03	1.013E+00	1.2E-03

Table 9 The predicted gauge readings and their uncertainties as obtained from Eqs. (12) and (14) for rotor 2.

p_t in Pa	p_{2PTB} in Pa	$u(p_{2PTB})$	p_{2CENAM} in Pa	$u(p_{2CENAM})$
3.0E-04	3.346E-04	5.4E-06	3.336E-04	1.7E-06
9.0E-04	1.003E-03	5.9E-06	1.001E-03	3.0E-06
3.0E-03	3.344E-03	9.7E-06	3.335E-03	7.3E-06
9.0E-03	1.005E-02	3.2E-05	1.001E-02	2.2E-05
3.0E-02	3.351E-02	1.1E-04	3.334E-02	7.2E-05
9.0E-02	1.003E-01	3.1E-04	9.999E-02	2.2E-04
3.0E-01	3.329E-01	5.6E-04	3.320E-01	5.8E-04
9.0E-01	9.858E-01	1.7E-03	9.837E-01	1.2E-03

The degree of equivalence between the two institutes can be tested using [10]

$$d_i = p_{iCENAM} - p_{iPTB} \tag{15}$$

for each target point and each transfer standard i. The uncertainty $u(d_i)$ is given by

$$u(d_i) = \sqrt{u^2(p_{iCENAM}) + u^2(p_{iPTB})}\ . \tag{16}$$

However, since this comparison covered 4 orders of magnitudes of pressure, the use of a ratio is more appropriate in order to get clear visualisation of the results. This ratio is defined as

$$r_i = \frac{p_{iCENAM}}{p_{iPTB}} \tag{17}$$

with

$$u(r_i) = \sqrt{\left(\frac{u(p_{iCENAM})}{p_{iCENAM}}\right)^2 + \left(\frac{u(p_{iPTB})}{p_{iPTB}}\right)^2}\ . \tag{18}$$

Herein p_{iCENAM} and p_{iPTB} are calculated by Eq. (12), $u(p_{iCENAM})$ and $u(p_{iPTB})$ by Eq. (14). The following table shows the result.

Table 10 The ratios $r_i = p_{iCENAM}/p_{iPTB}$ and their uncertainties as determined by Eq. (17) and (18). For u' see the following text.

p_t in Pa	r_1	r_2	$u(r_1)$	$u(r_2)$	$u'(r_1)$	$u'(r_2)$
3.0E-04	0.9953	0.9968	0.0288	0.0169	0.0286	0.0165
9.0E-04	0.9972	0.9975	0.0102	0.0066	0.0095	0.0056
3.0E-03	0.9970	0.9972	0.0043	0.0036	0.0029	0.0017
9.0E-03	0.9961	0.9956	0.0039	0.0039	0.0010	0.0008
3.0E-02	0.9957	0.9949	0.0039	0.0038	0.0006	0.0005
9.0E-02	0.9972	0.9964	0.0037	0.0037	0.0005	0.0004
3.0E-01	0.9980	0.9973	0.0024	0.0024	0.0004	0.0004
9.0E-01	0.9986	0.9978	0.0021	0.0021	0.0004	0.0004

If r_1 and r_2 are of the approximate same value significantly different from 1, this would clearly indicate a difference in the true generated pressures of the two standards. Generally, the values of r_1 and r_2 will be slightly different due to the scatter of the data. r_1 and r_2 are correlated, because the same standards j were used to determine σ_{1j} and σ_{2j}. In the Appendix it is outlined that a way to consider this correlation is to omit $u(p_{stj})$ in Eq. (7) for the determination of $u(\sigma_{ij})$ in Eq. (14). The respective value is called u' which is also listed in Table 10. The weighted mean r of r_1 and r_2 is then calculated for each target point by

$$r = \frac{r_1 / u'(r_1)^2 + r_2 / u'(r_2)^2}{1/u'(r_1)^2 + 1/u'(r_2)^2}. \tag{19}$$

The standard uncertainty of r at the respective target pressure p_t is

$$u(r) = \sqrt{\left(\frac{u(p_{stCENAM})}{p_{stCENAM}}\right)^2 r^2 + \left(\frac{u(p_{stPTB})}{p_{stPTB}}\right)^2 r^2 + 2\frac{(u_{T\sigma}(p_t))^2}{p_t^2} r^2 + \left(\frac{1}{u'^2(r_1)} + \frac{1}{u'^2(r_2)}\right)^{-1}}. \tag{20}$$

The first two terms under the square root describe the influence of the uncertainty of the pressure p_{stj} generated by each standard j that correlates to both r_1 and r_2, the third term the uncertainty contribution due to the temperature dependence of σ_{eff} as described before Eq. (13), and the last term in the bracket all other influences of Type A, which are due to the rotor instability, offset determination *RD*, temperature and scatter of data. Also for $u_{T\sigma}$ it is conservatively assumed that r_1 and r_2, and respectively σ_{1j} and σ_{2j}, are correlated by their temperature dependence of σ_{eff}.

With the quantity

$$d = r - 1 \tag{21}$$

the relative difference between the two primary standards apparent at this comparison is described, where

$$u(d) = u(r) \ . \tag{22}$$

Equivalence is generally assumed, if

$$d \leq 2u(d) = U(d) \tag{23}$$

or

$$|E_n| \leq 1 \tag{24}$$

with

$$E_n = \frac{d}{U(d)} \ . \tag{25}$$

The values generated from Eqs. (19) to (25) are summarised in the following table. Figure 3 presents d and $U(d)$ as functions of the target pressures in this comparison.

Table 11 The most condensed data as a result from this comparison. r is the ratio of the true generated pressures (inverse of the ratio of the calculated pressures at the same generated pressure) in the two standards (Eq. (19)), d is the relative difference between the pressures in the two standards (Eq. (21)), U(d) the expanded uncertainty (k=2) of d (see Eqs. (20), (22) and (23))and E_n as defined in Eq. (25).

p_t in Pa	r	d	$U(d)$	E_n
3.00E-04	0.9964	-0.0036	0.0295	-0.12
9.00E-04	0.9974	-0.0026	0.0120	-0.21
3.00E-03	0.9972	-0.0028	0.0070	-0.40
9.00E-03	0.9958	-0.0042	0.0077	-0.55
3.00E-02	0.9952	-0.0048	0.0076	-0.63
9.00E-02	0.9967	-0.0033	0.0074	-0.44
3.00E-01	0.9976	-0.0024	0.0048	-0.50
9.00E-01	0.9982	-0.0018	0.0041	-0.44

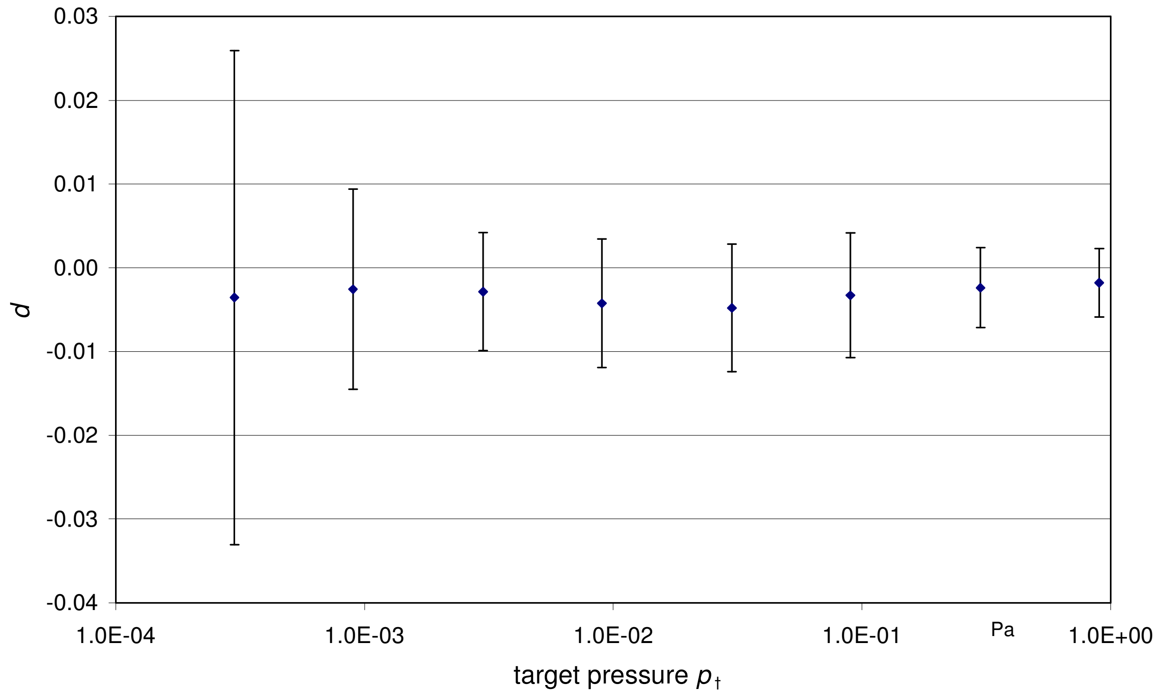

Figure 3 The relative difference $d = p_{CENAM}/p_{PTB}-1$ (Eq. (21)) of the two pressures generated in the two primary standards as a function of the target pressures in this comparison. Overlap of uncertainty bar with 0 means equivalence of the two standards.

12. Link to other key comparisons

There are three other comparisons to link the result of this comparison to: Euromet.M.P-K1.b, CCM.P-K4, and the CCM.P-K3 comparison with a range from $3 \cdot 10^{-6}$ Pa to $9 \cdot 10^{-4}$ Pa that was started before this RMO comparison. Measurement taking for CCM.P-K3 was finished in 2001. This comparison could create the link to the lowest two target pressures of this comparison. Draft A, however, is still in preparation.

The most meaningful and complete link can be done with Euromet.M.P-K1.b, since it was carried out with the same protocol and the same transfer standards. By knowing the ratio r of the true generated pressures it is possible to link the CENAM values completely to the Euromet reference value p_{eur} via the PTB primary standard. The assumed stability of the PTB primary standard for the two comparisons was substantiated by a check standard. By multiplying r with the pressure p_{PTB} obtained during Euromet.M.P-K1.b one obtains a fictive value for the pressure p_{CENAM} which can be compared with the Euromet reference value p_{eur}:

$$p_{CENAM} = r p_{PTB} \qquad (26)$$

with the uncertainty

$$u(p_{CENAM}) = p_{CENAM} \sqrt{\left(\frac{u(p_{stCENAM})}{p_{stCENAM}}\right)^2 r^2 + \frac{(u_{T\sigma}(p_t))^2}{p_t^2} r^2 + \left(\frac{1}{u'^2(r_1)} + \frac{1}{u'^2(r_2)}\right)^{-1}} . \tag{27}$$

The degree of equivalence can be evaluated by introducing

$$E_{n,euromet} = \frac{p_{CENAM} - p_{eur}}{2 \cdot \sqrt{u^2(p_{CENAM}) + u^2(p_{eur})}} \tag{28}$$

The following Table 12 gives the results.

Table 12 Link of the CENAM primary standard to the reference value p_{eur} of Euromet.M.P-K1.b. $E_{n,euromet}$ is related to a fictive CENAM pressure value during the Euromet.M.P-K1.b.

p_{CENAM}	$u(p_{CENAM})$	$E_{\text{n,euromet}}$	p_{PTB}	p_{eur}	$u(p_{\text{eur}})$
2.986E-04	4.348E-06	-0.15	2.997E-04	3.000E-04	8.1E-07
8.975E-04	4.917E-06	-0.24	8.998E-04	9.000E-04	1.8E-06
2.996E-03	7.712E-06	-0.23	3.004E-03	3.000E-03	5.2E-06
8.983E-03	1.983E-05	-0.34	9.021E-03	9.000E-03	1.6E-05
2.991E-02	6.450E-05	-0.53	3.005E-02	3.000E-02	5.5E-05
8.979E-02	1.940E-04	-0.42	9.009E-02	9.000E-02	1.5E-04
2.991E-01	5.120E-04	-0.74	2.998E-01	3.000E-01	3.6E-04
8.978E-01	1.063E-03	-0.72	8.994E-01	9.000E-01	1.1E-03

Since it was a result of Euromet.M.P-K1.b (see Draft B report, Section 12) that equivalence with the Euromet reference pressure at 0.9 Pa automatically means equivalence with the CCM.P-K4 reference value at 1 Pa (assuming that the same methods of calibration would be used for these two target pressures), it can be concluded that the CENAM primary standard is also equivalent to the CCM reference value at 1 Pa.

13. Discussion and conclusions

In the present comparison, the degree of equivalence between pressures generated by the vacuum primary standards of CENAM and PTB was tested. Both standards were fully equivalent in the range $3 \cdot 10^{-4}$ Pa up to 0.9 Pa. There is, however a systematic relative difference of the generated pressures of about $3 \cdot 10^{-3}$ where the generated pressure of CENAM is lower than the pressure PTB for the same gauge reading. A similar systematic difference for the CENAM pressure can also be observed by comparison with the EUROMET reference pressure. This could indicate that the truly generated pressure in the CENAM standard is somewhat lower than the calculated one. Since in comparison with the EUROMET reference values p_{eur} the $E_{n,euromet}$ of CENAM is higher towards higher pressures where the uncertainty contribution due to the transfer standards is lowest, this may indicate that the uncertainty of the generated pressure by CENAM is presently somewhat underestimated. It has to be emphasised, however, that there is full equivalence within $k = 2$ with p_{eur}.

Finally, it can be concluded that the assembly and evaluation of the high vacuum primary SEE1 of CENAM was successful.

14. Appendix

Suppose we have two measured quantities x_i (i=1, n=2) and would like to calculate the weighted mean y and its uncertainty $u(y)$ when the uncertainties $u(x_i)$are given.

If the x_i are all independent, the results are:

$$y = \frac{\sum_{i=1}^{n} \frac{x_i}{u^2(x_i)}}{\sum_{i=1}^{n} \frac{1}{u^2(x_i)}} \tag{29}$$

$$u^2(y) = \frac{1}{\sum_{i=1}^{n} \frac{1}{u^2(x_i)}} \tag{30}$$

When the x_i are correlated, the following notes may be useful. Suppose we have the model

$$x_i = \frac{p_i}{p_{st}} \tag{31}$$

and the p_i (relative uncertainty u_i) and p_{st} (u_0) are independent, so that

$$u^2(x_i) = u_0^2 + u_i^2 \tag{32}$$

(all uncertainties relative).

Under the assumption that

$$\frac{p_i^2 - p_i p_k}{p_{st}^2} << \frac{u_i^2}{u_0^2} \tag{33}$$

which is always the case in the calculations here, because $p_i \approx p_k$ the results are

$$y = \frac{\sum_{i=1}^{n} \frac{x_i}{u_i^2}}{\sum_{i=1}^{n} \frac{1}{u_i^2}} \tag{34}$$

$$u^2(y) = u_0^2 + \frac{1}{\sum_{i=1}^{n} \frac{1}{u_i^2}} \qquad (35)$$

These equations make the evaluations easier and better understandable.

15. References

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