REPUBLIC OF SLOVENIA
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METROLOGY INSTITUTE OF THE REPUBLIC OF SLOVENIA

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EURAMET project 1479 (EURAMET.M.FF-S14)
Inter-comparison of 1000 L proving tank

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Co-Pilot - Elsa Batista - IPQ

Final report

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Contents

1 Introduction

During the EURAMET TC Flow meeting held in Bern, Switzerland in April 2019, it was agreed to start a second comparison with a 1000 L proving tank. The aim of this project was to compare results and method calibration of this thank. Both gravimetric and volumetric method were used by several laboratories. This comparison allowed the participating laboratories to test the agreement of their results and uncertainties despite the different used equipment and different calibration methods.

The Slovenian National Metrological Institute, MIRS, acted as the pilot of this comparison and the Portuguese National Metrological Institute, IPQ was the co-pilot.

2 Participants

The project protocol was sent to all the EURAMET TC Flow members and 18 NMIs agreed to participate. During the comparison one NMI withdrew. The circulation of proving tank started in December 2019. Each NMI had one month to perform the measurements. The participants are presented in Table 1, in order of participation date.

Table 1 –Time schedule

Country, NMI	**Contact Person**	**Measurements date**
Portugal, IPQ	Elsa Batista	December 2019
France, LNE	Florian Beaudoux	January 2020
Czech Republic, CMI	Miroslava Benkova	June 2020
Lithuania, LEI	Gediminas Zygmantas	July 2020
Sweden, RISE	Per Wennergren	August 2020
Slovenia, MIRS	Urška Turnšek	September 2020
North Macedonia, BOM	Jovan Atanasovski	October 2020
Montenegro, MBM	Mirjana Mihailović	December 2020
Turkey, TUBITAK UME	Ümit AKÇADAĞ	January 2021
Norway, JV	Gunn Kristin Svendsen	February 2021
Moldova, INM-MD	Braguta Alexandru	March 2021
Spain, CEM	Carmen Sánchez	May 2021
Netherlands, VSL	Erik Smits	July 2021
Slovakia, SMU	Milan Mišovich	September 2021
Romania, INM-RO	Florin Istrate	October 2021
Austria, BEV	Anton Niessner	January 2022
Serbia, DMDM	Ljiljana Mićić	April 2022
Portugal, IPQ	Elsa Batista	June 2022

Due to custom issues and COVID-19 epidemics there were some delays in the original schedule and the measurements only finished in the June 2022.

3 Transfer standard

The 1000 L proving tank that was circulated in this comparison was supplied by IPQ and was specifically modified for this comparison, as this instrument was previous used in the 2013 EURAMET 1157 comparison.

Figure 1 – 1000 L proving thank

It is made as follows (see Figure 1):

- carbon steel construction
- 1000 L nominal volume at 20 °C
- double windows (glass plates) in the neck (front and back)
- scale extending from -1 % to +1 %, scale interval 0,01 %, with a length of 225 mm
- approximate mass excluding the transport box: 300 kg
- diameter of main body: 1,35 m
- height including the wheels: 2,40 m
- inner diameter of the neck: 330 mm
- coefficient of cubical thermal expansion of the TS: 0,0000335 °C^{-1}
- RTD (Pt-100) including read-out calibrated by IPQ, length: 300 mm

4 Calibration method

The participating laboratories used their normal calibration procedure in order to obtain the volume at the graduation mark of 1000 L. Both gravimetric (weighing of water) and volumetric methods (filling from one proving tank to another) could have been used.
The measurements were performed at varying room temperature conditions and the results recalculated for a reference liquid temperature of 20 °C.
After emptying the proving tank the laboratories had to wait 30 seconds before closing the valve. The valve should have been opened and closed just once.
In the spreadsheet that was supplied by the pilot of the comparison, each laboratory described the equipment that was used during the calibration and its traceability.

4.1 Type of calibration method

Both the gravimetric and volumetric method were allowed to be used. Seven laboratories used both methods, four laboratories used the volumetric method and six laboratories used the gravimetric method, see Table 2.

Table 2 – Used calibration method

NMI	Method
IPQ	Gravimetric
LNE	Gravimetric
CMI	Gravimetric
LEI	Gravimetric and volumetric
RISE	Gravimetric and volumetric
MIRS	Volumetric
BOM	Volumetric
MBM	Gravimetric and volumetric
TUBITAK UME	Gravimetric
JV	Gravimetric and volumetric
INM-MD	Gravimetric and volumetric
CEM	Volumetric
VSL	Gravimetric
SMU	Gravimetric
INM-RO	Volumetric
BEV	Gravimetric and volumetric
DMDM	Gravimetric and volumetric

4.2 Gravimetric method

The majority of laboratories that performed the calibration of the 1000 L proving tank with the gravimetric method used the formula described in ISO 4787:2021 [1]:

$$V_{20} = (I_L - I_E) \times \frac{1}{\rho_W - \rho_A} \times \left(1 - \frac{\rho_A}{\rho_B}\right) \times [1 - \gamma(t - 20)] \quad (1)$$

V_{20}	-	Volume, at 20 ºC, in L
I_L	-	Is the balance indication of the vessel loaded with water, in kg
I_E	-	Is the balance indication of the empty vessel, in kg (zero in case the balance was tared with the volumetric instrument or receiving vessel)
ρ_W	-	Is the density of water at t (in degrees Celsius), in kg/L,
ρ_A	-	Is the density of air, in kg/L
ρ_B	-	Is the density of balance weights used during measurement (substitution) or during calibration of the balance, assumed to be 8,0 kg/L
γ	-	Is the coefficient of cubic thermal expansion of the material of which the instrument under calibration is made, in 1/°C
t	-	Is the temperature of the water used in the calibration, in °C

Some laboratories used their own model and equation.

4.3 Volumetric method

The majority of the laboratories that performed the calibration of the 1000 L proving tank by the volumetric method used the formula described in Calibration Guide No. 21 [2]:

$$V_t = NV_0[1 - \gamma_{RS}(t_{0RS} - t_{RS}) + \beta(t_{SCM} - t_{RS}) + \gamma_{SCM}(t - t_{SCM})] + \Delta V \quad (2)$$

V_t	-	Volume of the standard capacity measure (SCM) at t/°C, in L
V_0	-	Volume of the reference standard (RS) at the reference temperature t_{0RS}, in L
t_{0RS}	-	Reference temperature of the RS, in °C
t	-	Reference temperature of the SCM, in °C
t_{RS}	-	Temperature of the liquid in the RS, in °C
t_{SCM}	-	Temperature of the liquid in the SCM, in °C
γ_{RS}	-	Coefficient of cubical thermal expansion of the material of the RS, in 1/°C
β	-	Coefficient of cubical thermal expansion of the liquid (water) at the average test temperature: 0,5 ($t_{RS} + t_{SCM}$), in 1/°C
γ_{SCM}	-	Coefficient of cubical thermal expansion of the material of the SCM, in 1/°C

Some laboratories used their own calibration model and equation.

5 Working conditions and equipment used

5.1 Gravimetric method

5.1.1 <u>Working conditions</u>

The working conditions in the laboratories of each participant using the gravimetric method are described in Table 3:

Table 3 – Gravimetric method working conditions

NMI	Temperature of water t_w/°C	Density of water ρ_w /(kg/L)	Air temperature t_a/°C	Atmospheric pressure *p*/hPa	Relative humidity RH/%
IPQ	20,54	0,99893	21,18	1004,2	70,4
LNE	20,35	0,99813	19,7	1010	29
CMI	24,67	0,99738	24,1	973,5	49,8
LEI	21,95	0,99810	21,7	1009	58
RISE	20,61	0,99818	22,8	1000,7	56,2
MBM	19,99	0,99821	20,5	1008,55	62,3
TUBITAK UME	15,638	0,99917	17,8	990,9	45,6
JV	3,1	0,99996	19,7	1012,2	22,3
INM-MD	18,69	0,99874	18,79	1008,99	52,78
VSL	21,44	0,99822	22,3	1009,19	98,8
SMU	20,99	0,99689	23,5	986,0	63,9
BEV	20,14	0,99834	20,25	1005,438	35,47
DMDM	14,03	0,99944	18,9	996,53	47,3

The majority of the laboratories used the PT 100 that was installed in the 1000 L proving tank for the water temperature measurements. The calibration certificate of the probe was supplied by IPQ and is attached Annex 2.

5.1.2 Type of water

The water production method and the formula or method used to determine the density of water are described in Table 4.

Table 4 – Working conditions of gravimetric method

NMI	Production method	Density formula
IPQ	Tap water	$-0,00520*x^2-0,00116*x+1000,53$
LNE	Deionized water	Tanaka formula
CMI	Tap water	Tanaka formula
LEI	Filtered tap water	Determined by density meter
RISE	Tap water	Tanaka formula

MBM	Distilled water	Tanaka formula
TUBITAK UME	Tap water	Determined by density meter
JV	Tap water	Tanaka formula
INM-MD	Tap water	Determined by density meter
VSL	Potable water	PTB 1990 (Spiweck, Bettin)
SMU	Tap water	ρ = -5,3571429* 10^{-6} * t_S * t_S + 7,5857143 * 10^{-6} * t_S + 1,0005931
BEV	Tap water	Determined by density meter
DMDM	Tap water	Determined by hydrometer

The water used by the majority of the laboratories is tap water. Corrections were applied for the impurity to the used water density formula in order to have the correct water density.

5.1.3 Mass standards

Some information about the type of mass standards used is given in Table 5.

Table 5 – Mass standards characteristics

NMI	**Manufacturer**	**Type**	**Upper range value *m*/kg**
IPQ	-	M1	1000
LNE	LNE LNE ZWIEBEL	tailored stackable mass tailored stackable mass F2 OIML	50/200 10 1g to 2
CMI	-	-	-
LEI	-	E2	20
RISE	RISE/Mettler/KMW	-	500
MBM	-	-	-
TUBITAK UME	Hafner	E2	1000
JV	Unknown	M1	500
INM-MD	ZWIEBEL	F1	20
VSL	-	1 x 1000 kg	1000
SMU	-	-	-
BEV	-	Rect. bar	20
DMDM	Hafner, Germany Majevica, Serbia Sartorius, Germany	F1 F1 F2	500 500 20

Only three laboratories used a mass standard of the same nominal volume as the calibrated proving tank.

5.1.4 Balance

Information about the type of balance used is given in Table 6:

Table 6 – Balance characteristics

NMI	Manufacturer	Type	Upper range value *m*/kg	Resolution *d*/g
IPQ	Mettler Toledo	KE1500	1500	20
LNE	Mettler Toledo	KC 600	600	0.1
CMI	Mettler Toledo	KES 3000	3000	10
LEI	Mettler Toledo	KES1500	1500	20
RISE	Mettler Toledo	KE2000	2500	1
MBM	Mettler Toledo	XP1003KM	1100	0,5
TUBITAK UME	TUBITAK UME	-	1200	10
JV	Unknown	Custom made	3200	0,2
INM-MD	Radwag	HRP 200.4Y.KO	200	0,2
VSL	Wöhwa	40	3500	20
SMU	Mettler	KG 6000	6000	10
BEV	Peuko	Mechanical comparator	1300	2
DMDM	Sartorius	CCS1000K	1510	5

The upper range and resolution of the balance is variable among laboratories and can influence the declared uncertainty. Two laboratories used balance with smaller upper range than nominal value of the calibrated proving tank.

5.2 Volumetric method

5.2.1 Working conditions

The working conditions as mentioned by the participants are described in Table 7:

Table 7 – Volumetric method working conditions

NMI	Temperature of water t_w /°C	Air temperature t_a /°C	Atmospheric pressure p/hPa	Relative humidity RH/%
LEI	22,55	22,5	1011	66,5
RISE	20,05	21,2	992,6	58,2
MIRS	18,47	23,2	992,9	67,1
BOM	18,10	17,8	1021	55,2
MBM	17,99	19,16	1023,4	50,7
JV	3,78	-	-	-
INM-MD	19,38	18,95	1012,30	45,16
CEM	19,65	21,5	935,83	54,2
INM-RO	20,99	21,04	1017,29	45,61
BEV	7,6	19,5	-	-
DMDM	14,48	18,9	1020,41	37,45

The majority of the laboratories used the PT 100 that was installed in the 1000 L proving tank for the water temperature measurements. The calibration certificate of the probe was supplied by IPQ and is attached in Annex 2.

5.2.2 Type of water

The majority of the laboratories used tap water. For the volumetric method the water impurity is not an issue for the calculations nor is it an uncertainty source for the results.

5.2.3 Volume standard

Information about the type of volume standard is reported in Table 8:

Table 8 – Volume standard

NMI	Manufacturer	Type	Volume V_0/L	Resolution/L
LEI	Etalon	M1p-200	200	0,0026
RISE	Furhoffs Rostfria AB	overflow	1000	20,3 ml/mm
MIRS	Aleksander Lozar	overflow	500	N/A
BOM	Edelstahlbau Tannroda GmbH	Ex	500	0,1
MBM	Edelstahlbau Tannroda Gmbh	To deliver	500	-
JV	Unknown	To deliver	1000	0,1
INM-MD	Ukraine	M1P-100 ГР-01	100	-
CEM	Vial-Metrologie	500 L Inox	500	-
INM-RO	Tehnometal	overflow	100	N/A
BEV	Lenhardt Metallbau	stripping plate	1000	N/A
DMDM	Justing	Overflow pipette	500	N/A

The majority of the laboratories used a 500 L standard constructed either as overflow or "to deliver".

6 Measurement results

6.1 Stability of the TS

IPQ acting as the co-pilot laboratory performed the calibration of TS at the beginning and at the end of the comparison. The final value was taken as the official result of IPQ. The results of stability measurements are presented in Table 9.

Table 9 – Stability of the TS

NMI	Measurement	Date	Volume x_i/L	Uncertainty $U(x_i)$/L	ΔV/L
IPQ	Initial	December 2019	999,38	0,16	**0,09**
IPQ	Final	June 2022	999,29	0,10	

The two results obtained by IPQ at the beginning and the of comparison are consistent. The difference in the measured volume is smaller than the stated uncertainty. This demonstrates that the TS had a stable volume during the entire comparison.

6.2 Measurement results

The measurement results presented by each participant are collected in Table 10.

Table 10 – Participants volume measurements

NMI	Gravimetric		Volumetric	
	Volume x_i/L	**Uncertainty** $U(x_i)$/L	**Volume** x_i/L	**Uncertainty** $U(x_i)$/L
IPQ	999,29	0,10		
LNE	999,33	0,14		
CMI	999,30	0,13		
LEI	999,35	0,18	999,38	0,20
RISE	999,29	0,11	999,33	0,14
MIRS			999,24	0,17
BOM			999,28	0,30
MBM	999,14	0,14	999,38	0,27
TUBITAK UME	999,70	0,20		
JV	999,27	0,16	999,35	0,27
INM-MD	999,37	0,17	999,34	0,21
CEM			999,22	0,18
VSL	999,22	0,099		
SMU	999,50	0,33		
INM-RO			999,82	0,47
BEV	999,215	0,060	999,208	0,065
DMDM	999,22	0,20	999,04	0,30
Mean value	**999,32**	**0,15**	**999,33**	**0,24**

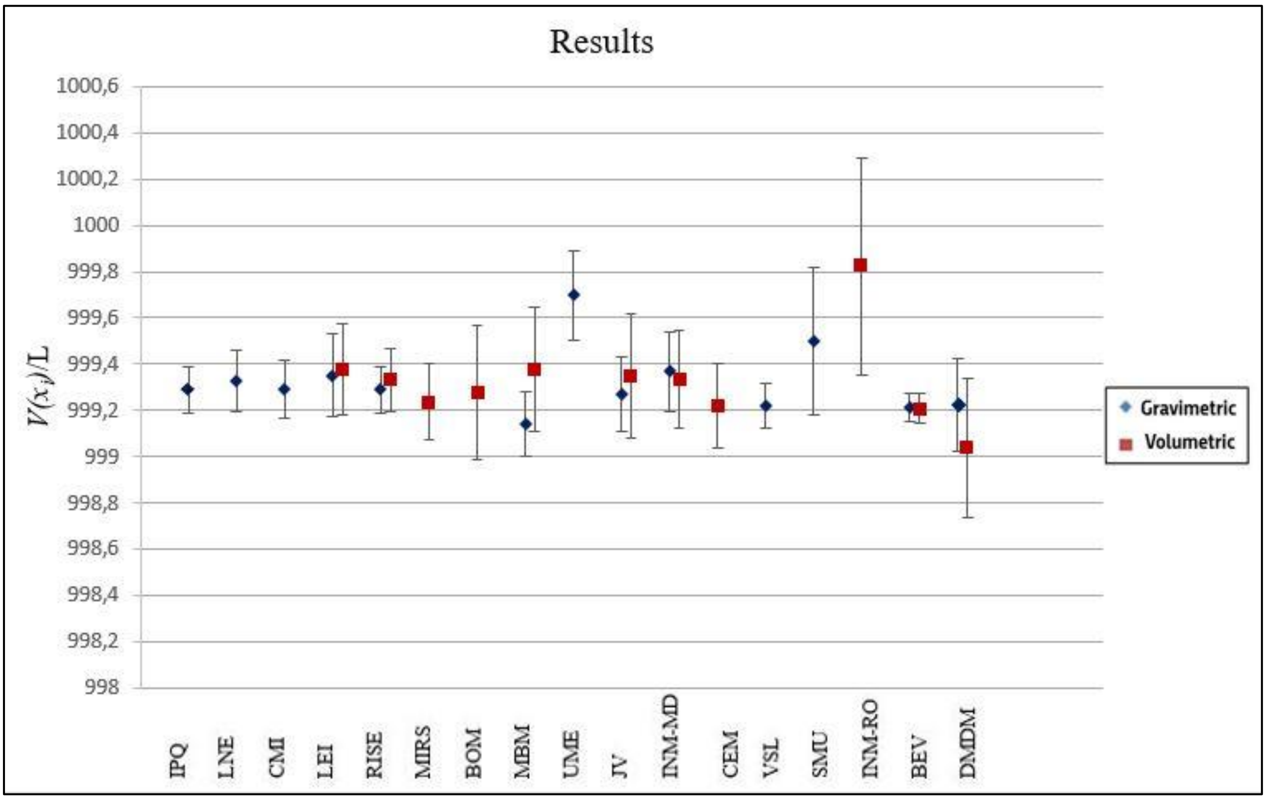

Figure 2 - Laboratory results

There are total of 24 measurements of 17 laboratories. For the laboratories that presented both volumetric and gravimetric results, only one was used for the determination of the reference value. The agreement between participants was, that the result with the lowest uncertainty is used.

There is no difference between the results from the gravimetric method and the results from volumetric method. The mean volume of gravimetric method is 999,32 L and of volumetric method is 999,33 L.

The presented uncertainties for the volumetric method are in all cases larger than for the gravimetric method, as expected, because volumetric method is a secondary calibration method.

6.3 Determination of the reference value

To determine the reference value y of this comparison (RV) the formula of the weighted mean was used, using the inverses of the squares of the associated standard uncertainty as the weights [3]:

$$y = \frac{x_1/u^2(x_1) + ... + x_n/u^2(x_n)}{1/u^2(x_1) + ... + 1/u^2(x_n)} \quad (3)$$

To determine the standard deviation $u(y)$ associated with y:

$$u(y) = \sqrt{\frac{1}{1/u^2(x_1) + ... + 1/u^2(x_n)}} \quad (4)$$

The expanded uncertainty of the reference value is $U(y) = 2 \times u(y)$.

To identify an overall consistency of the results a chi-square test can be applied to all *n* calibration results.

$$\chi^2_{obs} = \frac{(x_1 - y)^2}{u^2(x_1)} + \ldots + \frac{(x_n - y)^2}{u^2(x_n)} \quad (5)$$

where the degrees of freedom are: $\nu = n - 1$
The set of results is inconsistent when: $\Pr\{\chi^2(\nu) > \chi^2_{obs}\} < 0{,}05$. The function *CHIINV(0,05; n-1)* in MS Excel was used. The set of results is rejected when *CHIINV(0,05; n-1)* $< \chi^2_{obs.}$
If the consistency check has a positive result then *y* is accepted as the RV x_{ref} and $U(x_{ref})$ is accepted as the expanded uncertainty of the RV.
If the set of results appears to be inconsistent then the laboratory with the highest value of $\frac{(x_i - y)^2}{u^2(x_i)}$ is excluded from the next round of evaluation and the new reference value, reference standard uncertainty and observed chi-squared value is calculated again without the excluded laboratory. When the set or results pass the consistency check, the degree of equivalence d_i between each laboratory result x_i and the RV (x_{ref}) is calculated using the following formulas:

$$d_i = x_i - x_{ref} \quad (6)$$

$$U(d_i) = 2 \times u(d_i) \quad (7)$$

where $u(d_i)$ is calculated from:

$$u^2(d_i) = u^2(x_i) - u^2(x_{ref}) \quad (8)$$

Discrepant values can be identified when $|d_i| > 2u(d_i)$,
To calculate the degrees of equivalence d_{ij} between the laboratories the following formulas are used:

$$d_{i,j} = x_i - x_j \quad (9)$$

$$U(d_{i,j}) = 2 \times u(d_{i,j}) \quad (10)$$

Where $u(d_{i,j})$ is calculated from

$$u^2(d_{i,j}) = u^2(x_i) + u^2(x_j) \quad (11)$$

The factor 2 in equation (7) and (10) corresponds to a 95% coverage interval under the assumption of normal distribution of the results.
The normalized error $E_{n,i}$ describes the degree of equivalence of a laboratory *i* related to the RV.
$E_{n,i}$ was calculated for each reported value of the participant as follows,

$$E_{n,i} = d_i / U(d_i) \quad (12)$$

If $|E_{n,i}| \leq 1$, the measurement is generally considered as acceptable, and the measured values are consistent.

6.4 Results with reference value and RV uncertainty

The obtained reference value using the results of all 17 laboratories (ν = 16) is y = 999,270 L.
The expanded uncertainty $U(y) = 2 \times u(y)$ of the reference value is: 0,032 L.

The calculated value $\chi^2(\nu)$ = 26,30 is smaller than the observed χ^2_{obs} = 39,04, therefore consistency test fails. The result with highest value of $\frac{(x_i - y)^2}{u^2(x_i)}$ is TUBITAK UME. If the result of TUBITAK UME is removed, the consistency test with the remaining 16 laboratories ($\nu = 15$) passes, where expected $\chi^2(\nu)$ = 25,00 is bigger than the observed χ^2_{obs} = 18,94. Therefore, the newly calculated reference value (RV) is x_{ref} = 999,260 L. The expanded uncertainty $U(x_{ref})$ = 2 × $u(x_{ref})$ of the RV x_{ref} = 0,032 L.

All the measurement results, the reference value and its uncertainty are presented in the following Figure 3:

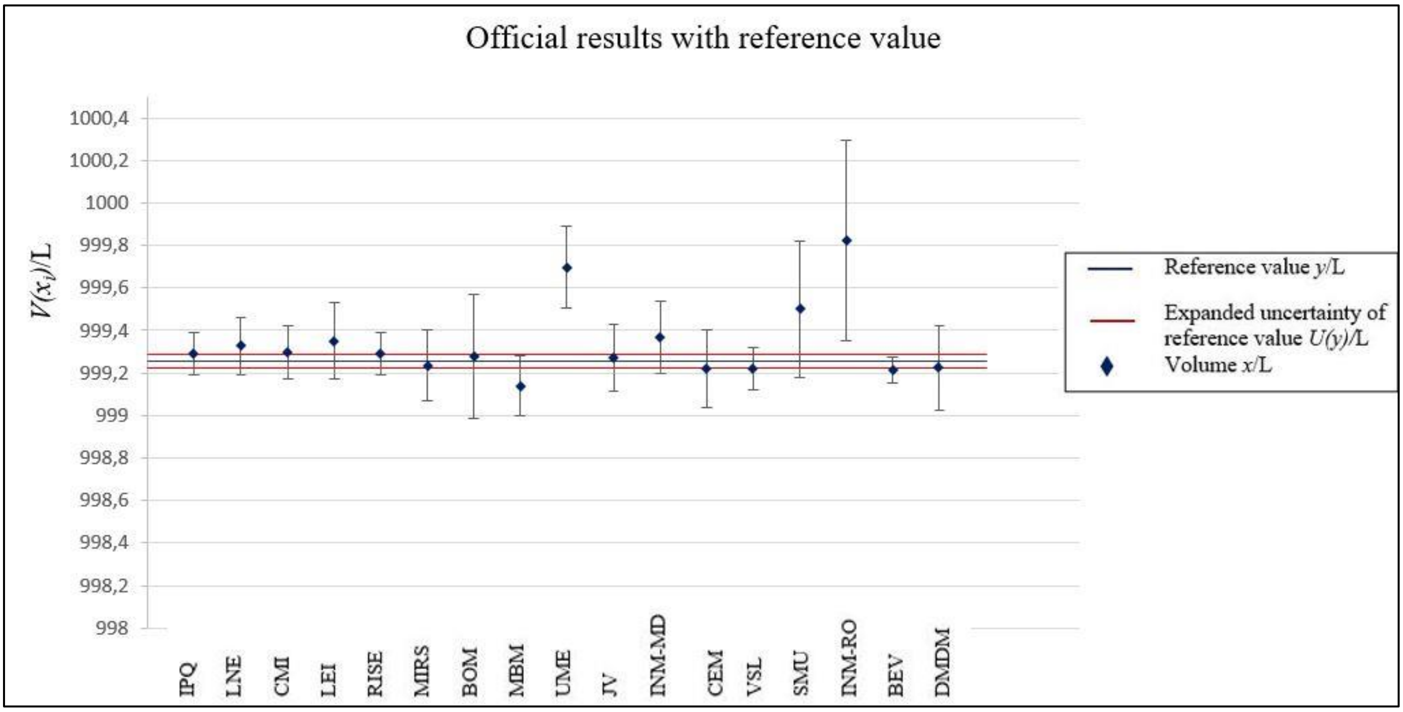

Figure 3 – Reference value and uncertainty

The degree of equivalence with the RV is presented in Figure 4 and Table 11:

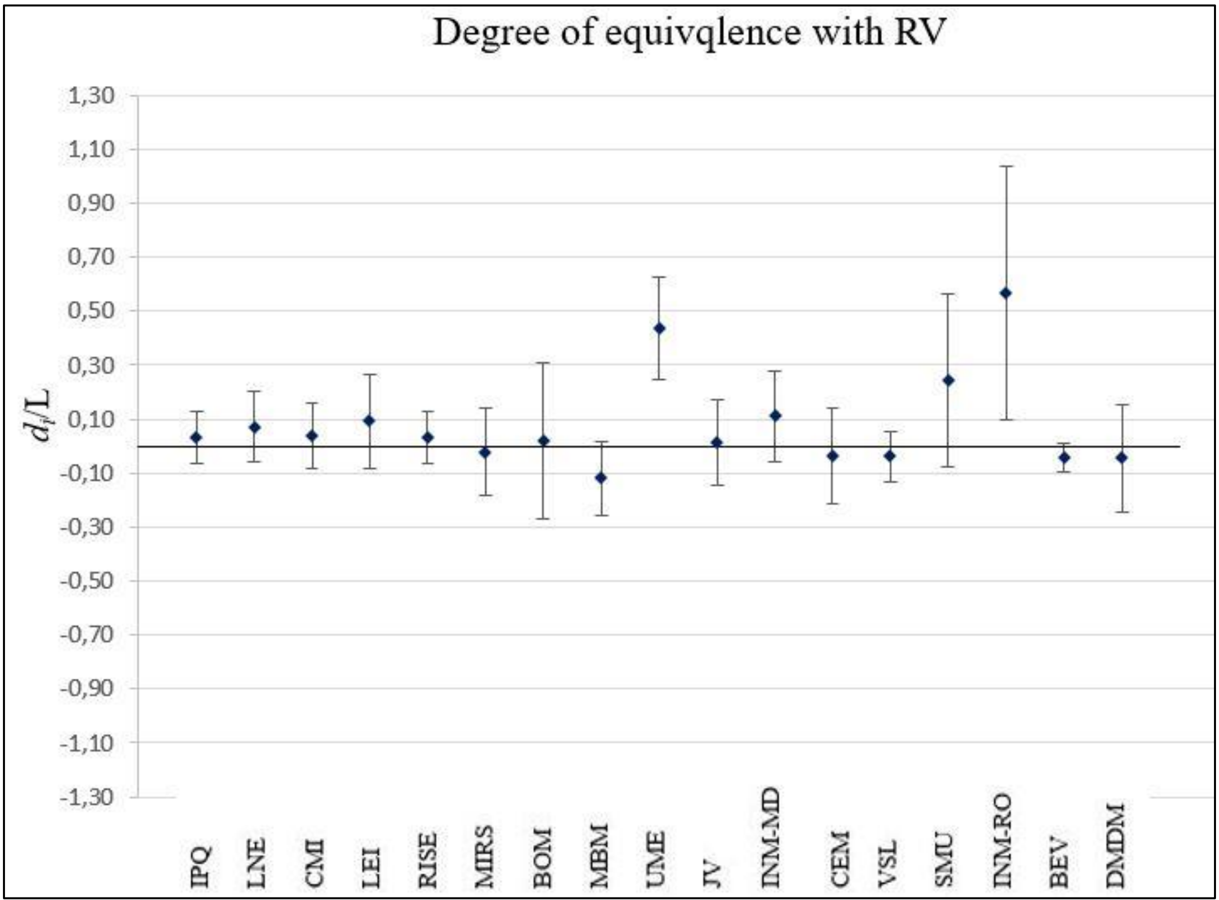

Figure 4 – Degree of equivalence with reference value

Table 11 – Degree of equivalence with RV

NMI	d_i	Ud_i/L	E_n
IPQ	0,03	0,09	0,33
LNE	0,07	0,13	0,54
CMI	0,04	0,12	0,30
LEI	0,09	0,18	0,52
RISE	0,03	0,10	0,34
MIRS	-0,02	0,16	-0,14
BOM	0,02	0,29	0,07
MBM	-0,12	0,14	-0,87
TUBITAK UME	0,44	0,19	2,30
JV	0,01	0,16	0,09

INM-MD	0,11	0,17	0,66
CEM	-0,04	0,18	-0,22
VSL	-0,04	0,09	-0,41
SMU	0,24	0,32	0,76
INM-RO	0,56	0,47	1,20
BEV	-0,04	0,05	-0,86
DMDM	-0,05	0,20	0,20

There is one more laboratory besides TUBITAK UME that present slightly discrepant value when compared with the reference value, that is INM-RO with a En=1,2, which is a warning level according to WGFF protocol.

The results of the degree of equivalence between all the laboratories can be found in Annex 3.

7 Uncertainty presentation

It was requested that all participants present their uncertainty calculations based on the GUM [4]. Because the used methods are different, also the uncertainty analysis will be different.

7.1 Gravimetric method

The uncertainty components for each NMI that used the gravimetric method are as follows:

Table 12 – Uncertainty components for gravimetric method

Uncertainty contributions	**NMI**												
	IPQ	LNE	CMI	LEI	RISE	MBM	UME	JV	INM-MD	VSL	SMU	BEV	DMDM
Repeatability measurements/L	9,6E-03	2,2E-02	6,0E-03	9,1E-03	2,1E-03	9,2E+00	1,2E-02	1,5E-02	2,5E-02	1,1E-02	1,7E-02	2,0E-02	3,2E-02
Mass/kg	2,8E-02	2,0E-03 3,0E-02	5,5E-02	1,6E-02	1,2E-02	6,9E+01	8,6E-02	3,1E-02	1,6E-03	1,6E-02	1,2E-01	1,0E-04	2,0E-03
Air Density /kgL^{-1}	9,6E-04	1,8E-02	1,3E-03	3,3E-04	7,6E-04	5,4E-01	5,8E-04	5,9E-04	5,8E-04	1,6E-06	2,3E-02	1,1E-03	3,4E-07
Water Density /kgL^{-1}	-2,9E-02	5,0E-04 2,5E-03	1,3E-02	3,5E-02	-3,3E-02	- 3,8E+00	2,9E-02	-1,5E-03	2,1E-02	9,3E-06	3,6E-02	-1,2E-02	-1,5E-08
Density of the mass pieces /kgL^{-1}	6,4E-04	-	5,3E-04	5,6E-04	2,3E-06 -9,5E-07 4,8E-04 -1,0E-04	1,3E+00	5,1E-04	1,4E-03	3,1E-04	-7,1E-06	5,3E-02	-5,6E-05	1,6E-06
Coefficient of expansion from the tank material/°C^{-1}	4,1E-04	-	1,4E-07	1,9E-03	-2,0E-03	1,1E-02	4,0E-03	1,6E-02	1,3E-03	-3,1E-06	4,3E-04	-3,70E- 04	5,8E-06
Water temperature /ºC	-7,1E-03	3,1E-02	3,5E-03	4,8E-03	2,6E-02	-5,2E-01	1,7E-02	-8,5E-03	1,3E-03	-1,7E-07	8,7E-02	-1,9E-03	-3,3E-07
Meniscus reading/L	2,5E-02	4,3E-02	2,5E-02	4,1E-02	1.8E-02	2,0E-01	2,5E-02	5,1E-02	2,9E-02	4,4E-02	2,6E-02	4,9E-03	3,0E-02
Other	-	2,5E-03	-	6,9E-02	-	-	-	-	7,4E-02	-	-	-	4,0E-02 8,1E-02
Combined Uncertainty/L	**0,049**	**0,067**	**0,062**	**0,089**	**0,051**	**0,48**	**0,096**	**0,078**	**0,086**	**0,050**	**0,161**	**0,024**	**0,10**

Expanded uncertainty/L	**0,10**	**0,14**	**0,13**	**0,18**	**0,11**	**0,14**	**0,20**	**0,16**	**0,17**	**0,099**	**0,33**	**0,06**	**0,20**

For the majority of the laboratories the largest uncertainty component is the uncertainty of the balance/mass and repeatability.

7.2 Volumetric method

The uncertainty components for the volumetric method are as follows:

Table 13 – Uncertainty components for volumetric method

Uncertainty contributions	**NMI**										
	LEI	RISE	MIRS	BOM	MBM	JV	INM-MD	CEM	INM-RO	BEV	DMDM
Repeatability measurements/L	2,6E-02	4,2E-03	2,9E-02	2,1E-02	2,7E-01	1,0E-02	1,5E-02	2,0E-02	3,4E-03	1,1E-02	1,02E-02
Volume standard/L	3,1E-02	4,6E-02	4,6E-02	3,5E-02	9,5E-02	1,01E-01	7,5E-02	5,0E-02	2,2E-01	2,1E-02	1,01E-01
Expansion coefficient of the standard/ºC^{-1}	5,3E-03	2,5E-04	1,1E-02	2,5E-06	-5,4E+00	1,3E-02	6,0E-04	-6,1E-04	2,5E-03	-1,7E-02	-8,19E-06
Temperature od the standard/ºC	3,0E-02	8,8E-03	2,6E-02	2,4E-02	-5,4E+01	6,8E-03	4,2E-03	-5,8E-02	4,3E-03	4,2E-03	-6,59E-07
Expansion coefficient of the water/°C^{-1}	8,6E-04	-1,3E-06	1,0E-03	2,0E-06	-10,0E-01	0,0E+00	4,7E-05	-3,9E-04	3,5E-05	-	-3,33E-08
Temperature of the proving tank/ºC	2,9E-02	5,8E-03	2,0E-02	3,1E-02	3,1E+01	-8,0E-03	4,2E-03	8,2E-03	1,5E-03	-	9,63E-07
Expansion coefficient of the tank/ºC^{-1}	2,4E-03	-1,4E-04	2,5E-03	1,7E-06	3,9E+00	2,7E-02	5,9E-04	7,5E-04	1,7E-03	1,2E-02	5,30E-06
Meniscus/L	4,1E-02	1.8E-02	2,5E-02	1,4E-02	2,6E+01	5,1E-02	4,6E-02	2,9E-02	4,5E-02	4,9E-03	2,89E-02
Evaporation/L	6,9E-02	2,6E-02	4,4E-02	2,6E-02	-	7,0E-02	2,6E-02	1,5E-02	7,0E-02	1,7E-03	4,04E-02
Other	6,1E-03	-	-	-	7,0E+01		4,4E-02	-	-	-	9,50E-02
Combined Uncertainty/L	**0,099**	**0,068**	**0,082**	**0,15**	**0,14**	**0,14**	**0, 11**	**0,086**	**0,24**	**0,033**	**0,15**
Expanded uncertainty/L	**0,20**	**0,14**	**0,17**	**0,30**	**0,27**	**0,27**	**0,21**	**0,18**	**0,47**	**0,065**	**0,30**

In the volumetric method the components with the largest contribution to the uncertainty are the volume standard calibration, the meniscus reading and the repeatability.

8 CMC

In order to assess the support of CMCs entries provided by this comparison Table 14 is provided.
For NMIs without CMC on this range, the label n/a is shown.

Table 14 - Consistency check for CMC entries for volume

NMI	Method	U_{CMCs} /%	$U_{1000\ L}$/%	Comments
IPQ	Gravimetric	0,010	0,010	Uncertainty claim consistent with CMC
LNE	Gravimetric	n/a	0,014	
CMI	Gravimetric	n/a	0,013	
LEI	Gravimetric	n/a	0,018	
RISE	Gravimetric	0,010	0,011	Uncertainty claim larger than CMC
MIRS	Volumetric	0,060	0,017	Uncertainty claim smaller than CMC
BOM	Volumetric	0,030	0,030	Uncertainty claim consistent with CMC
MBM	Gravimetric	n/a	0,014	
TUBITAK UME	Gravimetric	n/a	0,020	
JV	Gravimetric	0,020	0,016	Uncertainty claim smaller than CMC
INM-MD	Gravimetric	n/a	0,017	
CEM	Volumetric	0,020	0,018	Uncertainty claim smaller than CMC
VSL	Gravimetric	0,010	0,0099	Uncertainty claim smaller than CMC
SMU	Gravimetric	n/a	0,033	
INM-RO	Volumetric	n/a	0,047	
BEV	Gravimetric	0,0050	0,0060	Uncertainty claim larger than CMC
DMDM	Gravimetric	n/a	0,020	

9 Long-term stability of the proving tank

The 1000 L proving tank was first used as transfer standard in the intercomparison EURAMET 1157 in 2013. Its nominal volume has been changed for the purpose of this intercomparison by IPQ. We compared reference values from the first intercomparison in 2013 with reference value in this comparison (Table 14) and all the laboratory variation that participated in both comparisons (11), over time (Table 15).

Table 14 – Long-term stability of transfer standard – calculated reference value

Year	**Reference value/L**	$\Delta V_{2012\text{-}2022}$**/L**
2013	999,67	0,41
2022	999,26	

Table 15 – Long-term stability of transfer standard - laboratories

Laboratory	**Volume 2013 (L)**	**Volume 2022 (L)**	**ΔV 2013-2022 (L)**
RISE	999,700	999,291	0,41
MIRS	999,83	999,236	0,59
IPQ	999,55	999,29	0,26
BEV	999,705	999,215	0,49
CEM	999,73	999,22	0,51
VSL	999,620	999,22	0,40
SMU	999,64	999,50	0,14
DMDM	999,97	999,224	0,75
JV	999,64	999,272	0,37
BOM	999,52	999,28	0,24
LNE	999,55	999,33	0,22
		Average	**0,40**

The difference between reference value in 2013 and reference value in 2022 and the average of the laboratories that participated in both comparisons are similar, which proves a very good long- term stability of the proving tank.

10 Conclusions

The results are quite satisfactory. The majority of the laboratories present results that are consistent with the reference value, and with each other. Result from TUBITAK UME was not used to calculate reference value of this intercomparison. There is one more laboratory that present slightly discrepant value when compared with the reference value, that is INM-RO with a En=1,2 but still with the warning level.
The presented uncertainties for the volumetric method are in all cases larger that the uncertainties of the gravimetric method, as expected, because it is a secondary calibration method. The instrument tested has a very good long-term stability.

11 References

[1] EN ISO 4787:2021 Laboratory glass and plastic ware — Volumetric instruments — Methods for testing of capacity and for use

[2] Guidelines on the Calibration of Standard Capacity Measures Using the Volumetric Method EURAMET Calibration Guide No. 21 Version 2.1 (09/2021)

[3] M.G. Cox, The evaluation of key comparison data, Metrologia, 2002, Vol. 39, 589-595.

[4] JCGM 100:2008; Evaluation of measurement data — Guide to the expression of uncertainty in measurement (GUM), (09/2008)

Annex 1 - Spreadsheets

REPUBLIC OF SLOVENIA
MINISTRY OF ECONOMIC DEVELOPMENT AND TECHNOLOGY
METROLOGY INSTITUTE OF THE REPUBLIC OF SLOVENIA

Instituto Português da Qualidade

E-1479: EURAMET Project "Inter-comparison of 1000 L proving tank "

Data Form Gravimetric Calibration

General Information

Country		Laboratory	
Responsible		Date	

Technical specifications and traceability

Instrument	Manufacturer	Type	Range	Resolution	Calibration date	Traceability
Balance						
Weights						
Ambient air						
Temperature						
Pressure						
Relative Humidity						
Water						
Temperature						

	Production Method	Density formula (or table)
Water density		

Gravimetric used formula

Measurement procedure (short description)

Cleaning procedure

Comments:

Signature:

REPUBLIC OF SLOVENIA
MINISTRY OF ECONOMIC DEVELOPMENT AND TECHNOLOGY
METROLOGY INSTITUTE OF THE REPUBLIC OF SLOVENIA
Instituto Português da Qualidade

<u>F-1479: EURAMET Project "Inter-comparison of 1000 L proving tank "</u>

Results Form Gravimetric Calibration

Measurement results

Test	Mass of water m (kg)	Temperature of water t_w (°C)	Density of water ρ_w (kg/L)	Air temperature t_a (°C)	Atmospheric pressure P (hPa)	Relative humidity RH (%)	Density of air ρ_a (kg/L)	Volume $V_{20°C}$ (L)
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
							Mean (L)	
							Standard deviation (L)	

Uncertainty budget

Quantity (X_i)	Value (x_i)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient (c_i)	Uncertainty $u(y_i)$	Comment/ Explanation
Repetibility measurements						
Mass (kg)						
Air Density (kg/L)						
Water Density (kg/L)						
Density of the mass pieces (kg/L)						
Coefficient of expansion from the micropipette material (°C^{-1})						
Water temperature (°C)						
Meniscus reading (L)						
Other						
			Combined Uncertainty (L)			
			Degrees of equivalence			
			k			
			Expanded Uncertainty (L)			

Comments:

Signature:

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F-1479: EURAMET Project "Inter-comparison of 1000 L proving tank "

Data Form Volumetric Calibration

General Information

Country		Laboratory	
Responsible		Date	

Technical specifications and traceability

Instrument	Manufacturer	Type	Range	Resolution	Calibration date	Traceability
Volume standard						
Ambient						
Temperature						
Pressure						
Relative Humidity						
Water						
Temperature of laboratory volume standard						
Temperature of proving tank						

	Production Method
Water type	

Volumetric used formula

Measurement procedure (short description)

Cleaning procedure

Comments:

Signature:

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METROLOGY INSTITUTE OF THE REPUBLIC OF SLOVENIA
Instituto Português da Qualidade

F-1479: EURAMET Project "Inter-comparison of 1000 L proving tank "

Results form gravimetric calibration

Measurement results

Test	Temperature of water t_w (°C)	Air temperature t_a (°C)	Atmospheric pressure P (hPa)	Relative humidity RH (%)	Volume $V_{20°C}$ (L)
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
				Mean (L)	
				Standard deviation (L)	

Uncertainty budget

Quantity (X_i)	Value (x_i)	Distribution	Standard uncertainty) $u(x_i)$	Sensitivity coefficient (c_i)	Uncertainty $u(y_i)$	Comment/ Explanation
Repetibility measurements						
Volume standard [L]						
Expansion coeficient of the standard [°C⁻¹]						
Temperature od the standard [°C]						
Expansion coeficient of the waterL [C⁻¹]						
temperature of the proving tank [°C]						
Expansion coeficient of the proving tank [°C⁻¹]						
Meniscus [L]						
Evaporation [L]						
			Combined Uncertainty (L)			
			Degrees of equivalence			
			k			
			Expanded Uncertainty (L)			

Comments:

Signature:

Annex 2 – Calibration certificate of temperature probe

Instituto Português da Qualidade

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www.ipq.pt

CERTIFICADO DE CALIBRAÇÃO
CALIBRATION CERTIFICATE

NÚMERO 500.21/1942699
NUMBER

PAGINA 1 de 2
PAGE 1 of 2

ENTIDADE
ENTITY

NOME *NAME*	Instituto Português da Qualidade - Laboratório de Volume
ENDEREÇO *ADDRESS*	Rua António Gião, 2 2829-513 Caparica

INSTRUMENTO DE MEDIÇÃO
MEASURING INSTRUMENT

DESIGNAÇAO *DESIGNATION*	Termómetro de resistência de platina de 100 Ω	
	Sensor	Unidade de Leitura
MARCA *MANUFACTURER*	—	Tempcontrol
MODELO *MODEL*	—	P600
NÚMERO *SERIAL NUMBER*	T015	65010031333
CONSTITUIÇAO *COMPONENTS*	Termómetro de resistência de platina de 100 Ω com unidade de leitura	

CARACTERÍSTICAS METROLÓGICAS
METROLOGICAL CHARACTERISTICS

CLASSE DE EXATIDAO *ACCURACY CLASS*	—
INTERVALO DE INDICAÇAO *INDICATION INTERVAL*	—
RESOLUÇÃO DO DISPOSITIVO *RESOLUTION OF THE DISPLAYING DEVICE*	0,01 °C

OPERAÇÃO EFETUADA
OPERATION

TIPO *TYPE*	Calibração
DATA *DATE*	2019-10-04
MÉTODO *METHOD*	Calibração por comparação com termómetro padrão SMT15 em banho termoregulado.
DOCUMENTO DE REFERÊNCIA *REFERENCE DOCUMENT*	PT 5010095506
RASTREABILIDADE METROLÓGICA *METROLOGICAL TRACEABILITY*	Ao SI através da realização dos Pontos Fixos da EIT90 *SI Units through ITS90 Fixed Points*
INCERTEZA EXPANDIDA *EXPANDED MEASUREMENT UNCERTAINTY*	Ver páginas seguintes *See next pages*
RESULTADO DE MEDIÇÃO *MEASUREMENT RESULT*	Ver páginas seguintes *See next pages*

ISABEL MARIA MELO LOPES DIAS LÓIO — Assinado de forma digital por ISABEL MARIA MELO LOPES DIAS LÓIO Dados: 2019.10.08 08:46:44 +01'00'

RESPONSAVEL DE DOMINIO
TERMOMETRIA
Head of Thermometry Domain

João Luís Vieira Alves e Sousa — Assinado de forma digital por João Luís Vieira Alves e Sousa DN: c=PT, o=Instituto Português da Qualidade IP, cn=João Luís Vieira Alves e Sousa Dados: 2019.10.08 17:15:46 +01'00'

DIRETOR DA UNIDADE
LABORATÓRIO NACIONAL DE METROLOGIA
Director of the National Metrology Laboratory Unit

CIPM MRA

Este Certificado está de acordo com as Capacidades de Medição e Calibração (CMC), incluídas no Anexo C, do Acordo de Reconhecimento Mútuo (CIPM-MRA), redigido pelo Comité Internacional de Pesos e Medidas (CIPM). No âmbito do CIPM-MRA, todos os Laboratórios Nacionais participantes reconhecem reciprocamente a validade dos Certificados de Calibração e de Medição, emitidos para as grandezas, domínios e incertezas de medição, mencionados no Anexo C (para mais detalhes veja www.bipm.org).

This certificate is consistent with the capabilities that are included in Appendix C of the CIPM-MRA drawn up by the CIPM. Under the CIPM-MRA, all participating institutes recognize the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (for details see http://www.bipm.org).

RLNM43-01

Instituto Português da Qualidade

CERTIFICADO DE CALIBRAÇÃO
CALIBRATION CERTIFICATE

NÚMERO 500.21/1942699
NUMBER

PÁGINA 2 de 2
Page 2 of 2

CONDIÇÕES DE REFERÊNCIA: t = (20 ± 2) °C   *HR* = (50 ± 10) %
REFERENCE OPERATING CONDITION

RESULTADO:

Valor verdadeiro da temperatura	Indicação do termómetro T015	Incerteza Expandida
t_{ref} / °C	t / °C	t / °C
15,000	14,94	0,01
20,000	19,94	0,01
30,000	29,94	0,01

Notas:
O termómetro foi calibrado no Canal 1 da unidade de leitura

A incerteza expandida apresentada está expressa pela incerteza-padrão multiplicada pelo fator de expansão k = 2, o qual para uma distribuição normal corresponde a uma probabilidade expandida de 95 %, aproximadamente. A incerteza foi calculada de acordo com o documento Evaluation of Measurement Data - Guide to the expression of uncertainty in measurement, JCGM 100:2008 (GUM 1995 with minor corrections).

The reported expanded uncertainty is stated as the standard measurement uncertainty multiplied by the coverage factor k = 2, which for a normal distribution corresponds to a coverage probability of approximately 95 %. The uncertainty was calculated according to the document "Evaluation of Measurement Data - Guide to the expression of uncertainty in measurement, JCGM 100:2008 (GUM 1995 with minor corrections)".

RLNM43-01

Annex 3 – Degree of equivalence between the laboratories

di,j	IPQ	LEI	RISE	CMI	JV	UME	INM-MD	SMU	LNE	VSL	MBM	BEV	MIRS	BOM	CEM	INM-RO	DMDM
IPQ		-0,06	0,00	0,00	0,02	-0,41	-0,08	-0,21	-0,04	0,07	0,15	0,07	0,05	0,01	0,07	-0,53	0,07
LEI	0,06		0,06	0,06	0,08	-0,35	-0,02	-0,15	0,02	0,13	0,21	0,13	0,11	0,07	0,13	-0,47	0,13
RISE	0,00	-0,06		0,00	0,02	-0,41	-0,08	-0,21	-0,04	0,07	0,15	0,08	0,06	0,01	0,07	-0,53	0,07
CMI	0,00	-0,06	0,00		0,02	-0,40	-0,07	-0,21	-0,03	0,07	0,15	0,08	0,06	0,01	0,07	-0,53	0,07
JV	-0,02	-0,08	-0,02	-0,02		-0,42	-0,10	-0,23	-0,06	0,05	0,13	0,06	0,04	-0,01	0,05	-0,55	0,05
UME	0,41	0,35	0,41	0,40	0,42		0,33	0,20	0,37	0,48	0,56	0,48	0,46	0,42	0,48	-0,13	0,47
INM-MD	0,08	0,02	0,08	0,07	0,10	-0,33		-0,13	0,04	0,15	0,23	0,15	0,13	0,09	0,15	-0,45	0,14
SMU	0,21	0,15	0,21	0,21	0,23	-0,20	0,13		0,17	0,28	0,36	0,29	0,26	0,22	0,28	-0,32	0,28
LNE	0,04	-0,02	0,04	0,03	0,06	-0,37	-0,04	-0,17		0,11	0,19	0,11	0,09	0,05	0,11	-0,49	0,10
VSL	-0,07	-0,13	-0,07	-0,07	-0,05	-0,48	-0,15	-0,28	-0,11		0,08	0,00	-0,02	-0,06	0,00	-0,60	0,00
MBM	-0,15	-0,21	-0,15	-0,15	-0,13	-0,56	-0,23	-0,36	-0,19	-0,08		-0,08	-0,10	-0,14	-0,08	-0,68	-0,08
BEV	-0,07	-0,13	-0,08	-0,08	-0,06	-0,48	-0,15	-0,29	-0,11	0,00	0,08		-0,02	-0,06	0,00	-0,61	-0,01
MIRS	-0,05	-0,11	-0,06	-0,06	-0,04	-0,46	-0,13	-0,26	-0,09	0,02	0,10	0,02		-0,04	0,02	-0,59	0,01
BOM	-0,01	-0,07	-0,01	-0,01	0,01	-0,42	-0,09	-0,22	-0,05	0,06	0,14	0,06	0,04		0,06	-0,54	0,06
CEM	-0,07	-0,13	-0,07	-0,07	-0,05	-0,48	-0,15	-0,28	-0,11	0,00	0,08	0,00	-0,02	-0,06		-0,60	0,00
INM-RO	0,53	0,47	0,53	0,53	0,55	0,13	0,45	0,32	0,49	0,60	0,68	0,61	0,59	0,54	0,60		0,60
DMDM	-0,07	-0,13	-0,07	-0,07	-0,05	-0,47	-0,14	-0,28	-0,10	0,00	0,08	0,01	-0,01	-0,06	0,00	-0,60	

Discrepant values are found in red letters.