Final Report

EUROMET.M.FF-K4

Euromet Key Comparison for Volume Intercomparison of 100 ml Gay-Lussac Pycnometer

Based on the **EUROMET Project no. 692** conducted September 2002/ March 2004

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1. Introduction

The project for the comparison of the volume of 100 ml Gay-Lussac pycnometer was proposed initially in the Euromet TC Flow meeting 2002 in Prague. The protocol was based on BIPM Guidelines and sent to all the interested countries, 14 NMIs agreed to participate. The Euromet 692 project officially started in September 2002 and was concluded in March 2004.

The main purpose of the project was to compare the experimental method and the uncertainty calculation in the pycnometer volume determination and it was expected to be representative for all types of laboratory glassware.

In the Euromet TC Flow 2006 in Lisbon it was decide to propose this project as a Euromet Key Comparison due to the good overall agreement found.

2. Participants and schedules

Each laboratory was responsible for receiving the pycnometer, performing the measurements and sending it to the next laboratory according to the schedule.

Table 1 – List of participants in the Key Comparison on 100 ml pycnometer

Country	Laboratory	Contact	Date
Portugal	IPQ	Elsa Batista ebatista@mail.ipq.pt	September 2002
Czech Republic	CMI	Tomas Valenta tvalenta@cmi.cz	November 2002
France	BNM-LNE	André Gosset Andre.Gosset@lne.fr	January 2003
Denmark	FORCE	Lene S. Kristensen lsk@force.dk	February 2003
Germany	PTB	Heinz Fehlauer Heinz.Fehlauer@ptb.de	March 2003
The Netherlands	NMi-VSL	Erik Smits fmsmits@nmi.nl	April 2003
Slovakia	SLM	Miroslava Benkova Benkova@smu.gov.sk	May 2003
Turkey	UME	Ûmit Akcadag Umit.akcadag@ume.tubitak.gov.tr	June 2003
Spain	CEM	Antonio Puyuelo puyuelo@mfom.es	July 2003
Italy	IMGC	Salvatore Lorefice S.lorefice@imgc.cnr.it	September 2003
Hungary	OMH	Csilla Vámossy c.vamossy@omh.hu	November 2003
Greece	EIM	Zoe Metaxiotou zoe@eim.org.gr	December 2003
Austria	BEV	Ulrike Fuchs U.Fuchs@metrologie.at	January 2004

Sweden	SP	Peter Lau Peter.lau@sp.se	March 2004

3. The transfer package

The transfer standard consists on a pycnometer currently used for the measurement of the density of different liquids (from water to high viscosity paints). In order to have a correct density measurement the volume of the pycnometer must be obtained by calibration. Usually the calibration method is a gravimetric method.

There are several types of pycnometers. The one suggested for this comparison is a Gay-Lussac borosilicate glass pycnometer of 100 ml (with a coefficient of thermal expansion of $10\times10^{-6}C^{-1}$). The main reasons for choosing this type of pycnometer were:

- easy handling;
- the volume cannot be changed unless breaking the instrument;
- easy cleaning;
- possibility to observe air bubbles is evident.

This pycnometer has two different parts, the flask and the stopper. The dimensional requirements are described in ISO 3507:1999 [1].

During the comparison it was necessary to use two pycnometers because the first one (nº 62) was broken and replaced by nº 144.

Figure 1- Pycnometer nº 62

Figure 2 - Pycnometer nº 144

4. Conditions selected

The participating laboratories determined the volume of the contained water of a 100 ml glass Gay-Lussac pycnometer, at a reference temperature of 20 ºC.
A visual inspection of the outer and inner surface of the standard (including the stopper) was made when the standard arrived at the participating laboratory and the results noted on the corresponding sheets (see annex 1), IPQ, as the pilot laboratory received information if any damage occurred on the pycnometer.
After the measurements were concluded each participant send the equipment to the following laboratory and the corresponding results to the pilot laboratory.

5. Experimental procedure

The suggest method to determined the volume of the pycnometer was the gravimetric one. The following formula described in ISO 4787 [2] can be used for the calculation of the contained volume at the reference temperature of 20 ºC:

$$V_{20} = (m_2 - m_1) \times \frac{1}{r_W - r_A} \times \left(1 - \frac{r_A}{r_B}\right) \times \left[1 - g\,(t - 20)\right] \qquad (1)$$

Some laboratories used their own model and equation but they all applied gravimetric techniques to determine the volume of the pycnometer performing at least 10 measurements under repeatability conditions.

5.1. Experimental conditions

The ambient conditions were described by all participants.

Table 2 - Ambient conditions

Laboratory	Air Temperature (°C)	Pressure (hPa)	Humidity (%)	Air density (g/cm^3)	Water Temperature (°C)
IPQ-1	20,0	1006,3	60,0	0,00119	19,9
CMI	21,4	981	53	0,00116	21,8
BNM	20,24	1010,24	35,3	0,00120	20,001
FORCE	21,3	1025	64	0,00121	21,19
PTB-1	19,83	1016,61	41,1	0,00121	20,001
IPQ-2	19,8	1016,4	46,9	0,00120	19,7
PTB-2	19,63	1019,72	43,8	0,00121	20,001
NMi-VSL	21,2	1007,41	46,3	0,00119	21,51
SML	23,0	975	58	0,00115	21,81
UME	20,36	992,786	50,39	0,00117	20,834
CEM	20,044	936,332	46,79	0,00111	19,989
IMGC	20,24	988,499	53,6	0,00117	20,318
OMH	22,5	1003,01	32,9	0,00118	20,006
EIM	23,2	1012	34,5	0,00119	22,9
BEV	21,2	986,16	25,3	0,00117	20,007
SP	22	1006,5	37	0,00119	21,8
IPQ-3	20,5	1003	66	0,00120	20,4

Because this comparison lasted 18 months it is normal to see some differences in pressure, humidity or temperature. Nevertheless there were some problems with the determination of the volume in situations of low humidity that caused static electricity, and raised the uncertainty of the measurement.

5.2. Equipment

Each laboratory described the equipment used in the measurements and the respective traceability. For the majority of the laboratories the equipment used had the following characteristics:

Table 3 – Equipment characteristics

Equipment	Type	Range	Resolution
Balance Water thermometer	Electronic Digital	(0 - 1109) g (-50 to +420) ºC	(0,001 - 0,00001) g (0,001 – 0,1) ºC
Air thermometer	Digital	(-40 to +80) ºC	(0,001 - 0,1) ºC
Barometer	Digital	(0 - 1600) hPa	(0,001 - 1) hPa
Hygrometer	Digital	(0 - 100) %	(0,01 – 0,1) %

The columns for range and resolution indicate the minimum and the maximum values in the instruments used by the laboratories. The various equipments are described in more detail in Annex 2.

5.3. Type of water

The water should have the quality suitable for the purpose of calibration. The participants were asked for some water characteristics in order to evaluate its quality.

Table 4 – Water characteristics

Laboratory	Type	Density reference	Conductivity (µS/cm)
IPQ	Distilled	Bettin	3,86
CMI	Distilled	Bettin	-
BNM-LNE	Bi-distilled	Tanaka	-
FORCE	Distilled	Bettin	1,39
PTB	Super pure water	Bettin	0,056
NMi-VSL	Double distilled	Bettin	-
SLM	Distilled	Bettin	0,1
UME	ULTRAPURE	Kell	0,15
CEM	Electro deionised	Tanaka	-
IMGC	Bidistilled	Bigg (ITS-90)	-
OMH	Deionised Water	OMH2 solid density standard	-
EIM	Ultrapure	Wagenbreth	0,73
BEV	Deionised Water	DMA 5000	-
SP	Ultrapure	Bettin	<0,1

All participants used at least distilled water; the countries who presented conductivity values are all according to the ISO 3696 [3] < 5µS/cm.

The majority utilized the Bettin formulas for the density. This does not seems to influence the volume measures because we have laboratories with similar results using different formulas but in the future some harmonization must be imposed.

6. Analysis of the results

6.1. Volume measurements results

Two sets of results are presented because the first pycnometer was broken after the participation of five laboratories.

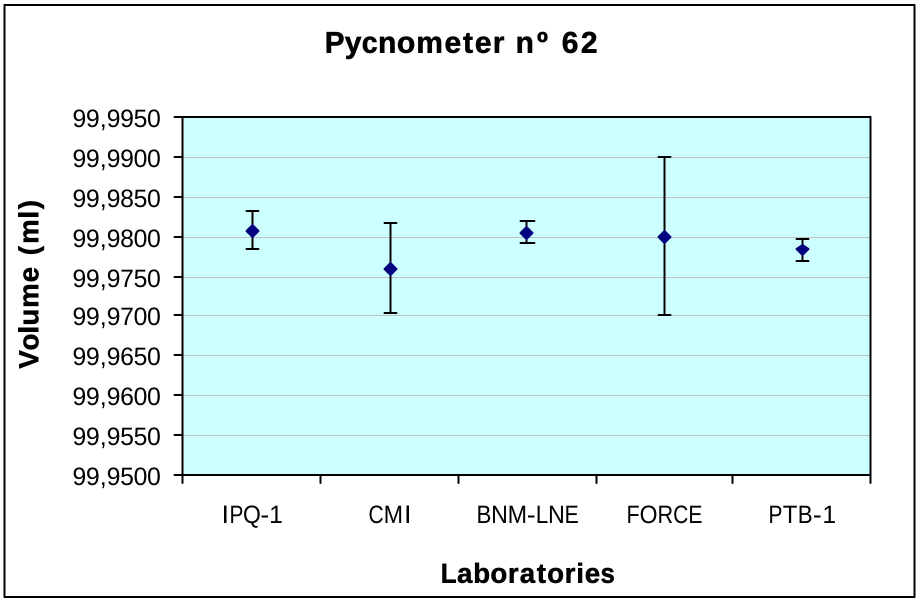

Figure 3 – Volume of Pycnometer nº 62

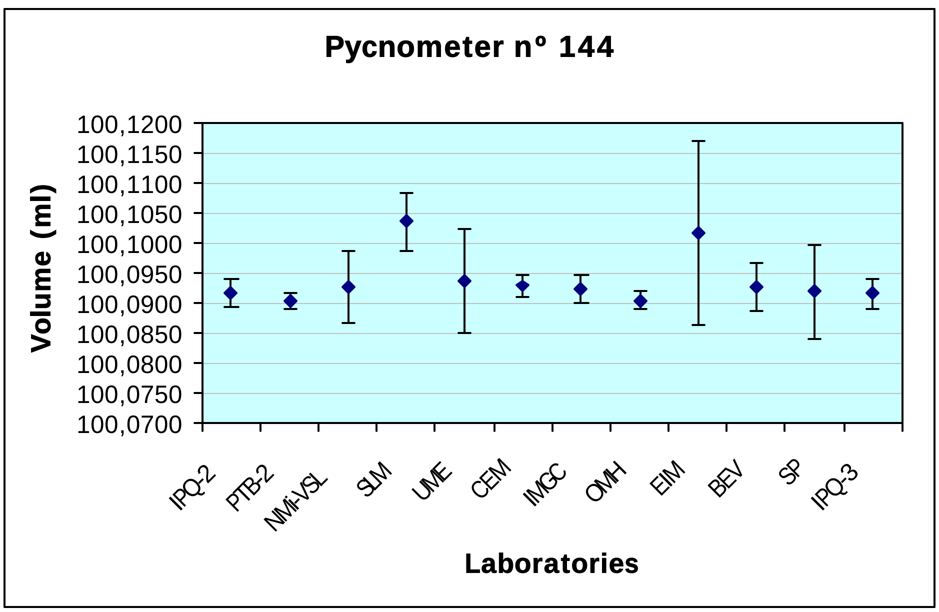

Figure 4 – Volume of Pycnometer nº 144

In order to compare the two groups of results a correction was applied to the results of the first pycnometer.

The correction was obtained averaging (weighted mean) the difference of the values obtained by the laboratories that performed the calibration of both pycnometers, PTB and IPQ.

Table 5 - Correction of the volume

	Difference (ml)	Weighted mean (ml)	Uncertainty (ml) with *k*= 2
IPQ	0,1109 **(IPQ-1 – IPQ-2)**	0,1118	0,0016
PTB	0,1120 **(PTB-1 – PTB-2)**		

This value 0,1118 ml was then added to the determined volume of all the laboratories that performed the calibration of the pycnometer nº 62 and a table and a figure with all the results can be presented.

Table 6 – Corrected volume results

Laboratory	Volume (ml)	Uncertainty (ml) with *k*=2
IPQ-1	100,0926	0,0025
CMI	100,0878	0,0056
BNM-LNE	100,0924	0,0014
FORCE	100,0918	0,0100
PTB-1	100,0901	0,0013
IPQ-2	100,0917	0,0024
PTB-2	100,0903	0,0012
NMi-VSL	100,0926	0,0060
SLM	100,1035	0,0046
UME	100,0936	0,0086
CEM	100,0928	0,0017
IMGC	100,0922	0,0024
OMH	100,0904	0,0016
EIM	100,1017	0,0154
BEV	100,0927	0,0041
SP	100,0920	0,0078
IPQ-3	100,0915	0,0026

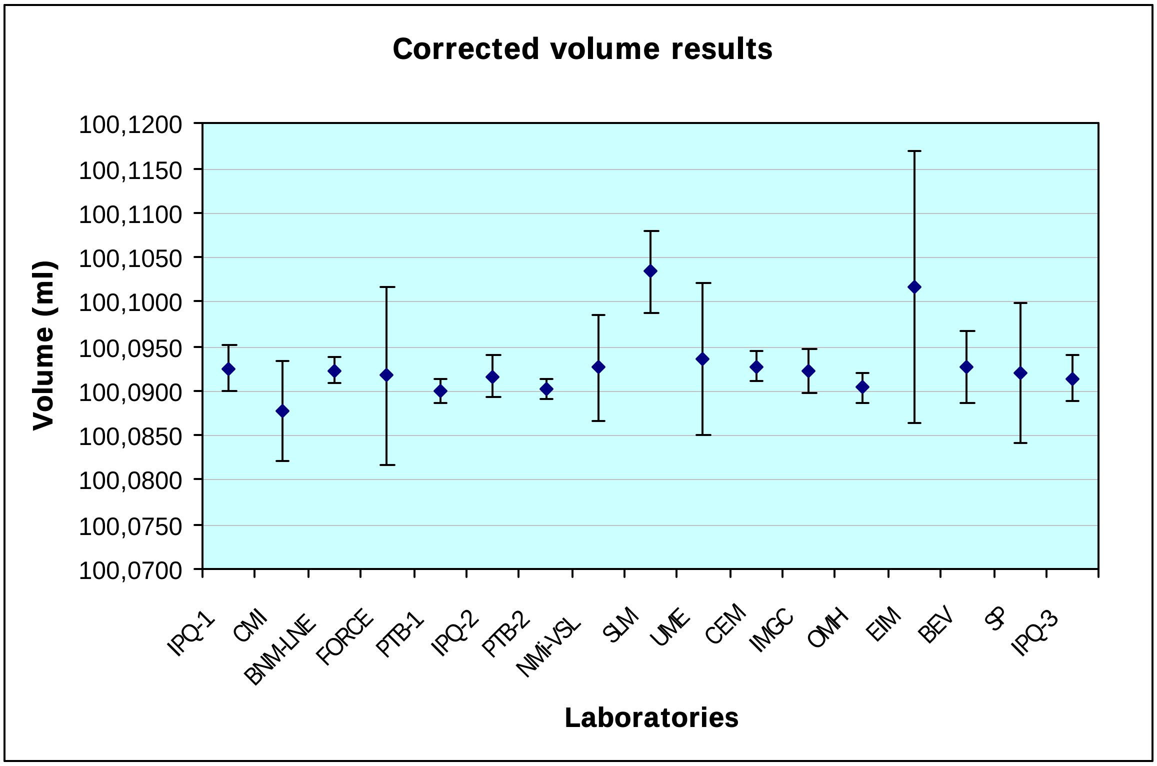

Figure 5 – Corrected volumes for all the participants

There are a total of 17 measurements of 14 laboratories. PTB performed two measurements with each pycnometer (nº 62 and nº 144) and IPQ performed 3 measurements: at the beginning, the middle and at the end of the comparison.

6.2. Determination of the reference value

To determine the reference value the formula of the weighted mean was used, using the inverses of the squares of the associated standard uncertainty as the weights [4]:

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

For the calculation of the reference value only one result for each laboratory was used, the chosen result for IPQ is IPQ-2 and for PTB is PTB-2.

6.3. Determination of the reference value uncertainty

To determine the standard deviation *u(y)* associated with *y* [4]:

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

(3)

6.4. Consistency statistical test - Chi-square test

To identify the inconsistent results a chi-square test can be applied to all results [4].

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

(4)

where the degrees of freedom are: $n = N - 1$

Regard the consistency check as failing if: $\Pr\left\{c^2(n) > c^2_{obs}\right\} < 0{,}05$

Table 7 – Consistency test

Laboratory	**Volume (ml)**	$c^2_{i\ obs}$ $\frac{(x_n - y)^2}{u^2(x_n)}$
IPQ	100,0917	0,0007
CMI	100,0878	1,9359
BNM-LNE	100,0924	1,0118
FORCE	100,0918	0,0004
PTB	100,0903	5,2019
NMi-VSL	100,0926	0,0964
SLM	100,1035	26,4622
UME	100,0936	0,2018
CEM	100,0928	1,7721
IMGC	100,0922	0,1962
OMH	100,0904	2,5141
EIM	100,1017	1,7061
BEV	100,0927	0,2532
SP	100,0920	0,0072

The obtained weighted mean using the 14 laboratories is

y = 100,0917 ml with a $u(y)$ = 0,0006 ml with k=2

The chi-square test gives the following results:

$c^2(0{,}05;13) = 22{,}3620$; $c^2_{obs} = 41{,}3602$

The consistency test fails. The value for $c^2_{SLM} = 26{,}4622$ is higher then $c^2(0{,}05;13) = 22{,}3620$. The volume value for the SLM is then removed from the weighted mean calculation and a new consistent test is performed.

The results now are the following:

$c^2(0{,}05;12) = 21{,}0261$; $c^2_{obs} = 14{,}3879$

We conclude that the results are consistent and y is the calculated reference value x_{ref} and $u(y)$ the standard uncertainty $u(x_{ref})$.

x_{ref} = 100,0914 ml, $u(x_{ref})$ = 0,0006 ml with k=2

In the figure 6 it is shown the measurement results, the calculated reference value and its uncertainty.

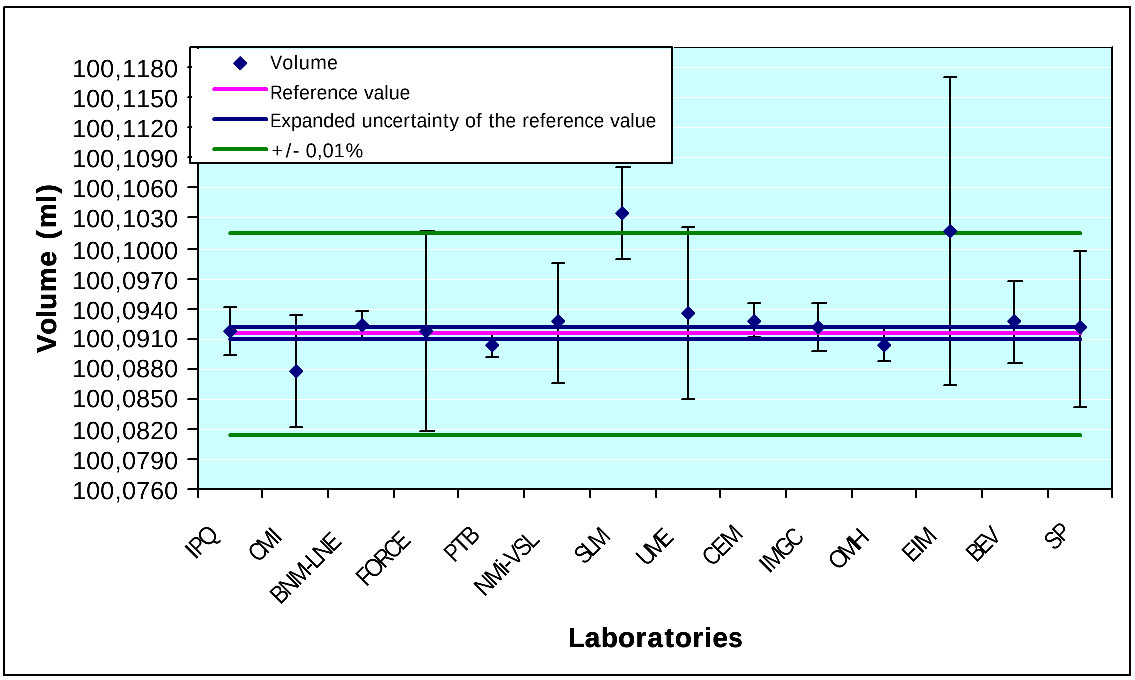

Figure 6 – Participant results compared with reference value

All measurement results are quite close except for the SLM result that has been removed from the weighted mean calculation and the EIM result, due to problems with the humidity and the procedure that were referred by EIM.

6.5. Degrees of equivalence

To calculate the degrees of equivalence between the reference value and the laboratories the following formula is used [4]:

$d_i = x_I - x_{ref}$ (5)

and $U(d_i) = 2u(d_i)$ (6)

were $u(d_i)$ is given by

$u^2(d_i) = u^2(x_i) - u^2(x_{ref})$ (7)

The factor 2 in (6) gives 95% coverage under the assumption of normality.

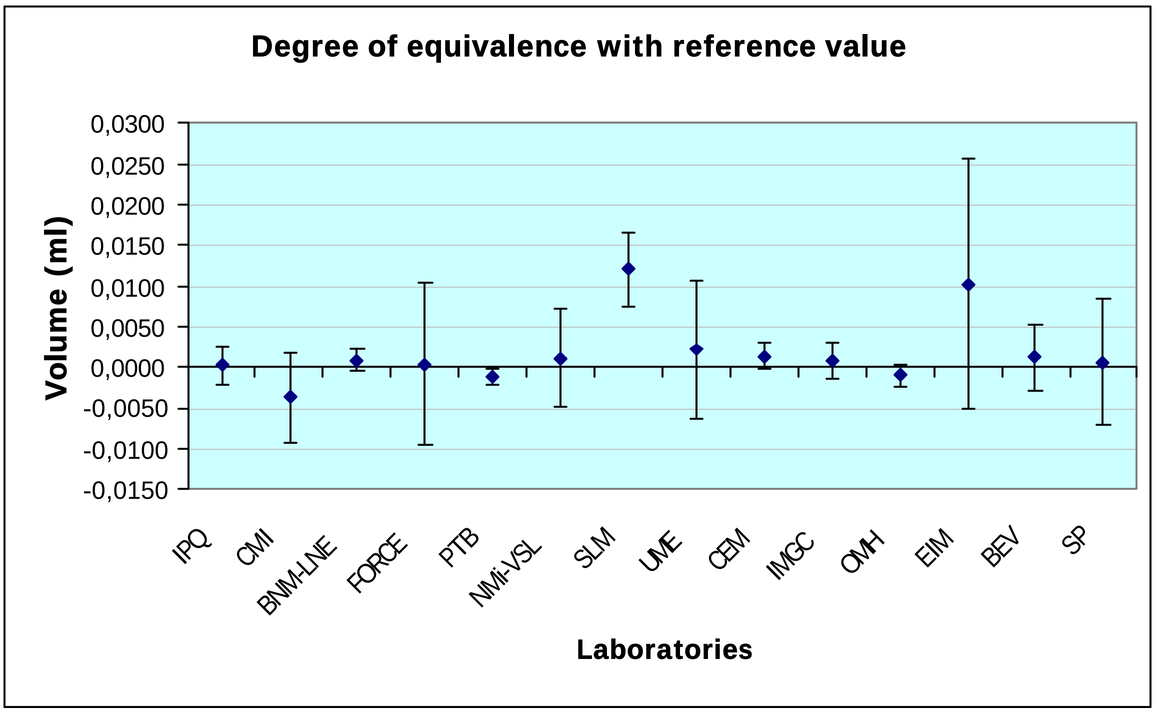

Figure 7 – Degree of equivalence between the laboratory and the reference value

The degree of equivalence between the majority of the laboratories and the reference is quite good, except for one or two cases.

The degree of equivalence between the laboratories can also be calculated using:

$d_{i,j} = x_i - x_j$ (8)

$U(d_{i,j}) = 2u(d_{i,j})$ (9)

Where $u(d_{i,j})$ is given by

$$u^2(d_{i,j}) = u^2(x_i) + u^2(x_j) \quad (10)$$

The results are presented in the table of Annex 3. The uncertainty is with a coverage factor of $k = 2$ presen ted in the lower part of the matrix.

In this table we can have a general idea of the differences in the volume results between the laboratories.

7. Uncertainty presentation

7.1. Type A and type B uncertainty

It was requested that all participants presen t the systematic and random standard uncertainties.

All the presented uncertainties are expanded uncertainty with a cover factor of 2.

Because of some confusion in defining the random uncertainty it was decided to present in this report the standard deviat ion of the mean of the determined volume instead.

Figure 8 presents the different opinions on the achieved measurement uncertainty. The standard deviation of the mean from 10 repeated measurements was taken as the type A contribution. The remaining uncertainty components of type B comprise the combination on a standard level. The total uncertainty is the value specified by the laboratories themselves on an expanded confidence level of 95 %.

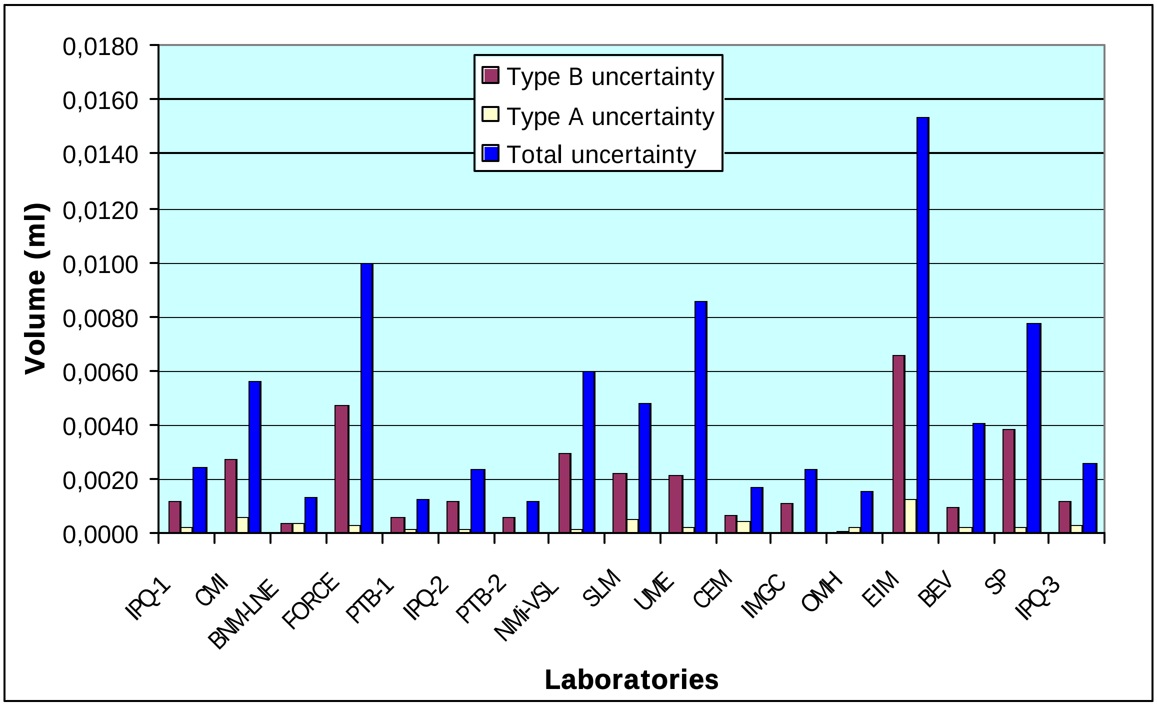

Figure 8 - Difference between the type A and type B uncertainty

The laboratories PTB, IMGC, IPQ and NMi-VSL have very low spread in the measurements and Force, SP, EIM and NMi-VSL have very high type B contributions.

7.2. Uncertainty components

A spreadsheet (Annex 1) with the proposed uncertainty components was presented to all participants and the majority of the laboratories replied according to this proposal.

The proposed uncertainty components were: mass, mass pieces density, water density, air density, expansion coefficient and temperature. The results for the mass are only referring to the values of the mass of the filled standard.

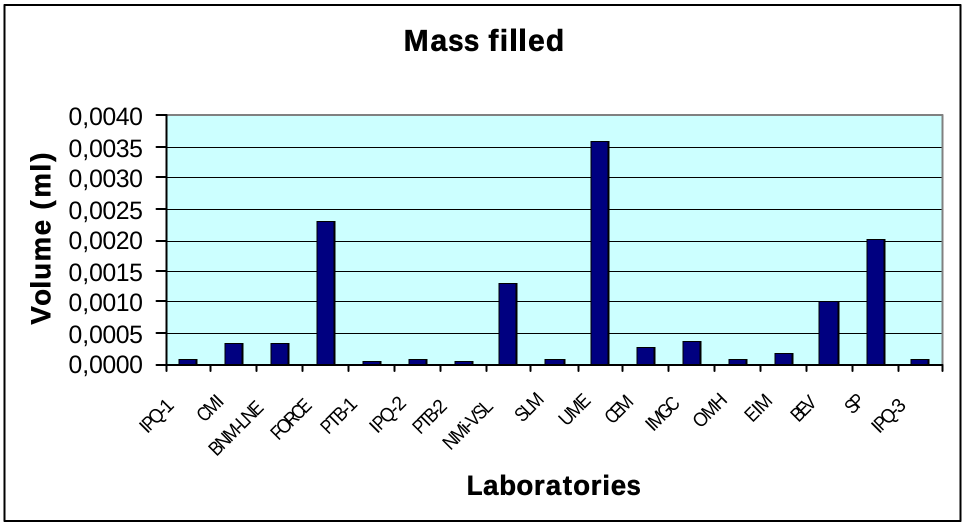

Figure 9 – Mass filled uncertainty

These uncertainties values probably include the whole of the weighing procedure for the mass filled, so the major difference between the results may be due to several components like the used mass standards or the static electricity.

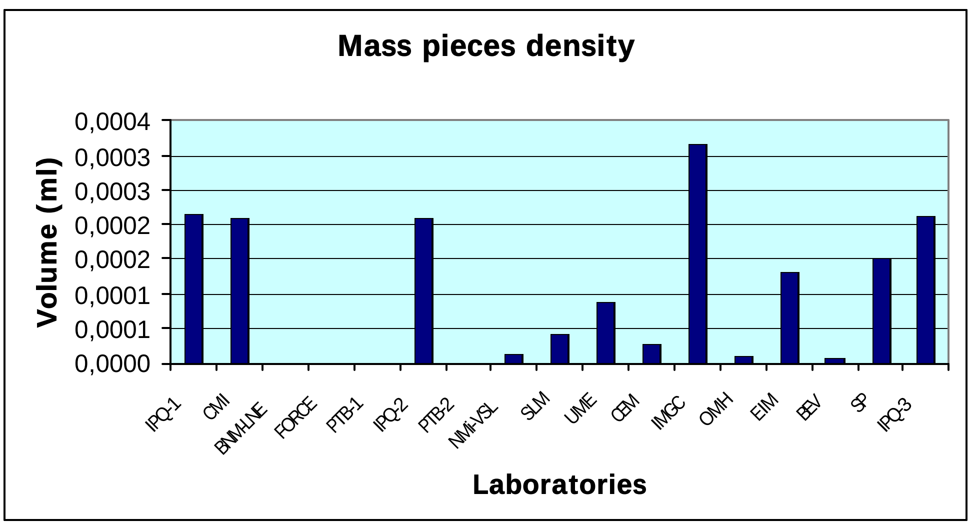

Figure 10 – Mass pieces density uncertainty

Some laboratories do not consider this uncertainty, probably this component is added into the mass filled uncertainty.

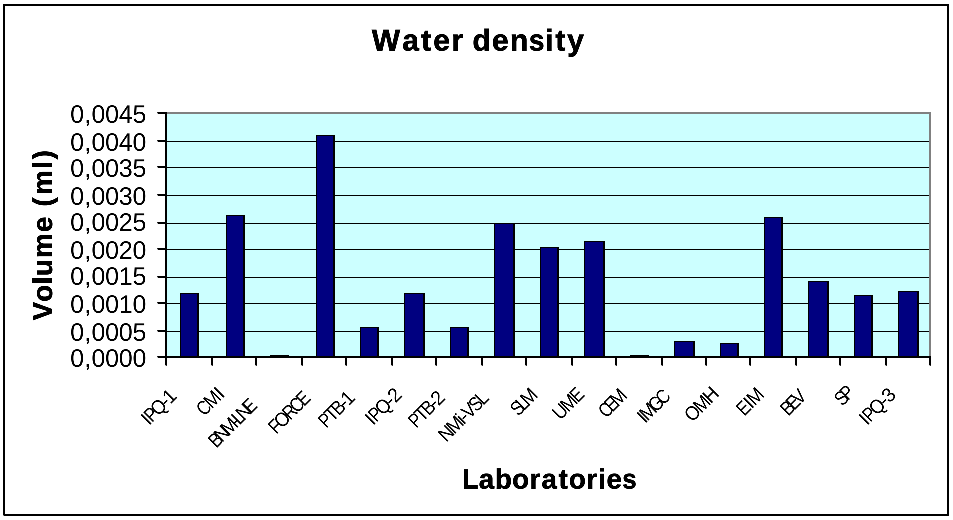

Figure 1 1 – Water density uncertainty

All the laboratories have specified a value; the lower values probably are due to the purity of the water or some different way of determining the density of the water. Also some laboratories may have put of this contribution into the temperature uncertainty.

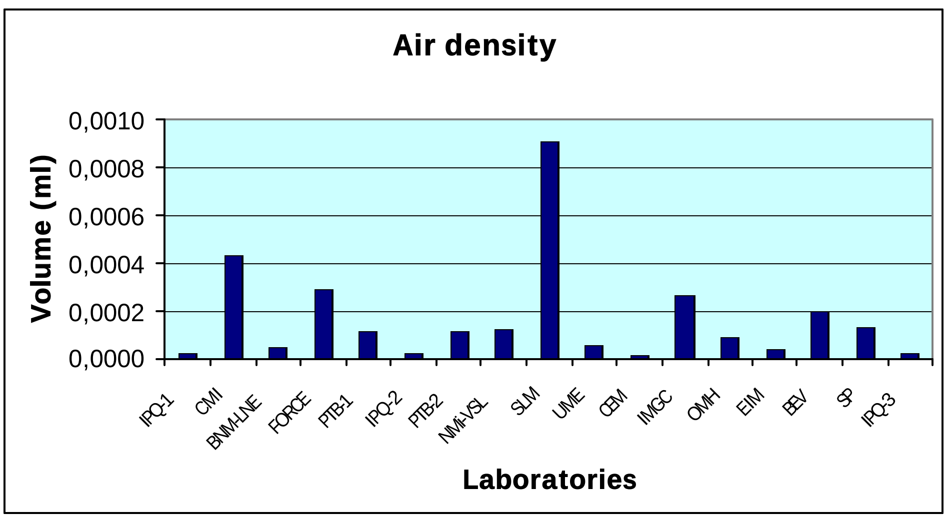

Figure 12 – Air density uncertainty

The uncertainties between the laboratories are quite similar only one laboratory has stated a very high value compared to the others.

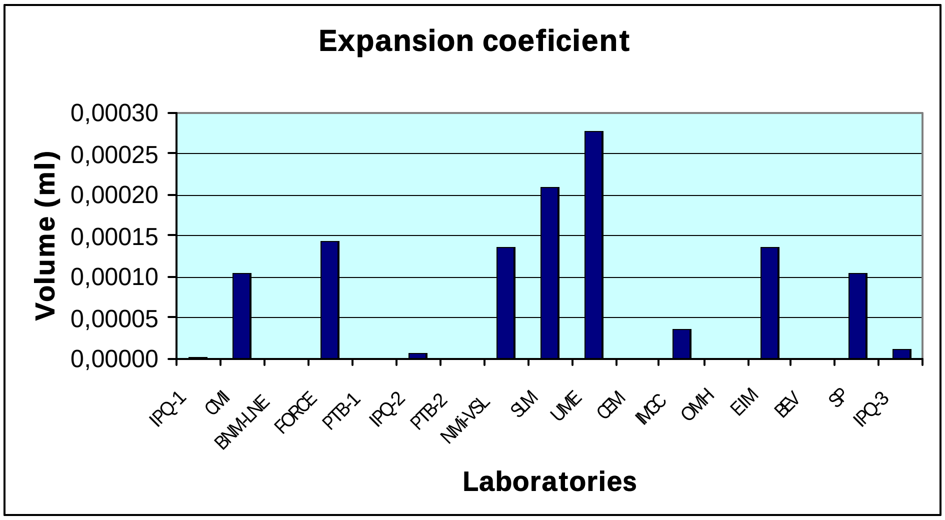

Figure 13 – Expansion coefficient uncertainty

Several laboratories do not question the expansion coefficient and others have very low values.

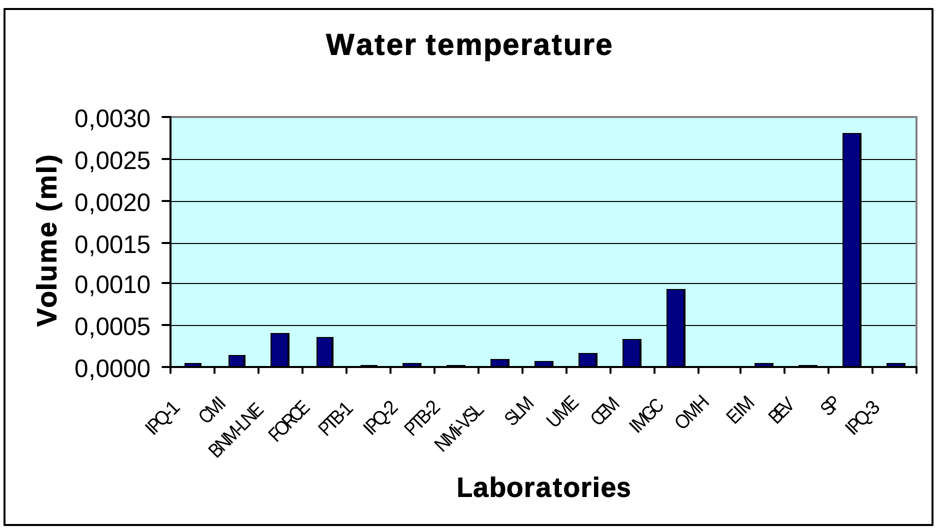

Figure 1 4 – Water temperature uncertainty

The uncertainty of the water temperature is very similar between the laboratories; only SP has a large uncertainty because they use a standard value for all the volume standards that they calibrate.

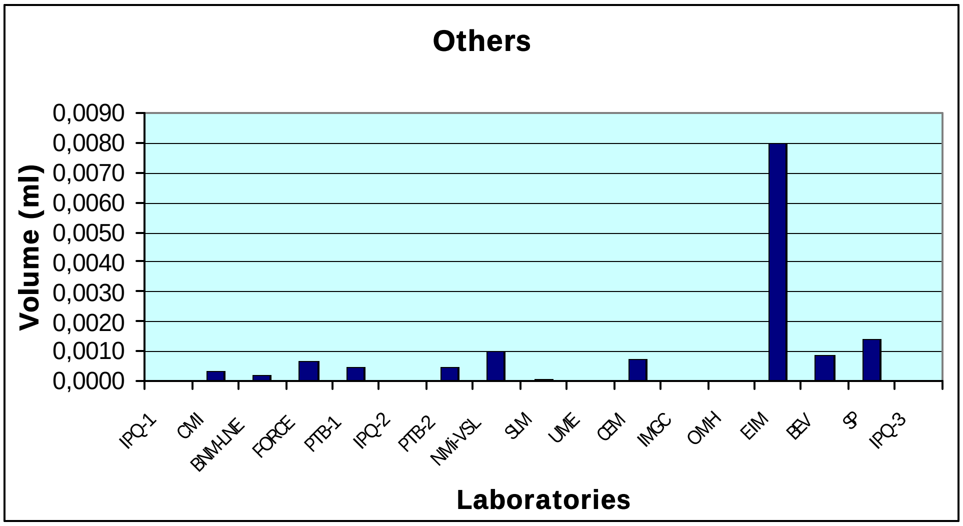

Figure 1 5 – Other uncertainty components

Some laboratories presented uncertainties components in addition to those proposed in the spreadsheet by the pilot laboratory; in each case the different components were added in order to present a single result. Some different components are: the pycnometer temperature, the cleaning of the remaining water of the stopper, or the static electricity, weight differences, mass empty, etc.

The use of a different equation models on the calculation of the contained volume may be the cause for some of the observed differences in the results of the uncertainties, mainly for the water temperature and water density.

The uncertainty components for each laboratory are defined in greater detail Annex 4.

7.3. Major source of uncertainty

Table 7 – Major source of uncertainty

Laboratory	Major source of uncertainty
IPQ-1	Water density
CMI	Water density
BNM-LNE	Water temperature
FORCE	Water density
PTB-1	Water density
IPQ-2	Water density
PTB-2	Water density
NMi-VSL	Water density
SLM	Water density
UME	Mass
CEM	Other
IMGC	Water temperature
OMH	Water density
EIM	Water density
BEV	Water density
SP	Water temperature on water density
IPQ-3	Water density

It can be seen in this table that the major source of uncertainty for almost every laboratory is the water density. Most laboratories prepare the water, but almost none has the possibility to determine its density by direct measurement. Instead, the laboratories generally use the measured temperature and calculate the density according to one of the density formulas (references) given in table 4. Depending on the judgment, how close the prepared water is to the one on which the density fo rmula is based on, the uncertainty will have a large influence on the total calibration uncertainty.

7.4. Average of the components for the standard uncertainties

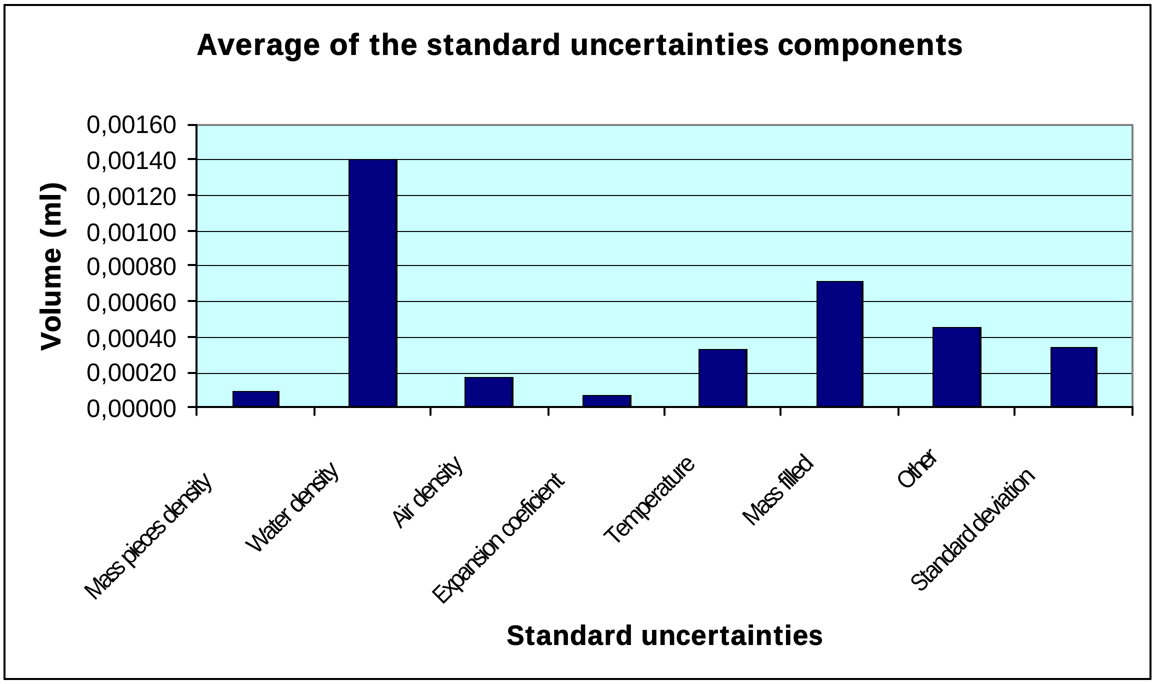

Figure 16 – Average of the standard uncertainty components

The previous figure represents averaged values over all laboratories for the main uncertainty components. As can be seen the major source of uncertainty is considered to be the water density followed by the mass determination.

8. Conclusions

This comparison involved 14 laboratories at all, and lasted one and half year.

One of the major risks was to break the glass pycnometer, witch actually happened after 5 measurements. Replacing the pycnometer and adding a correction to the first 5 volume results resolved the problem.

Globally the results are quite satisfactory. Except for one or two participants, the laboratories volume results are quite consistent with the reference value, and with each other.

The uncertainty budgets are very similar and the major uncertainty component to the final uncertainty is, for the majority of the participants, the water density.

There is a difference in the determination of the total uncertainty in some of the participants. It is probably due to the repeatability of the measurements, problems with the ambient conditions, the use of different mass standards and the use of different formulas for the volume calculation.

Some laboratories reported damages in the pycnometer that could influence the volume result, but at the end of the comparison the pilot laboratory examined the pycnometer and concluded that the reported defect existed already at the beginning of the comparison. The results were confirmed with the last measurement of the volume of the pycnometer by the pilot laboratory.

9. References

1. ISO 3507 - Laboratory glassware - Pyknometers, Genève 1999;

2. ISO 4787 - Laboratory glassware - Volumetric glassware - Methods for use and testing of capacity; Genève 1984;

3. ISO 3696 – Water for analytical laboratory use: specification and test methods Genève, 1987;

4. M.G. Cox, “The evaluation of key comparison data”, Metrologia, 2002, Vol. 39, 589-595.

Annex 1 – Spreadsheet

Instituto Português da Qualidade
PORTUGUESE INSTITUTE FOR QUALITY

EUROMET Project "Volume calibration of 100 ml Gay-Lussac Pycnometer"

Data Form

General Information

Country		Laboratory	
Responsible		Date	

Equipment

	Type	Range	Resolution
Weighing instrument			
Thermometer			
Barometer			
Hydrometer			
Other equipment			

Other Informations

	Type	Density reference	Measured conductivity
Water			

	Type	Density(g/ml)
Mass standards		

Used volume calculation formula:

Cleaning and drying the pycnometer:

Comments:

Signature:

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EUROMET Project "Volume calibration of 100 ml Gay-Lussac Pycnometer"

Results form

Ambient Conditions

Air temperature (ºC)	
Pressure (hPa)	
Humidity (%)	
Air Density (g/ml)	

Measurement results

Test number	Instrument mass empty (g)	Instrument mass filled (g)	Water temperature (ºC)	Volume (ml)
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
Mean value				
Standard deviation				

Uncertainty budget

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty $c_i \times u(x_i)$	Degrees of Freedom υ_i
Mass (g)					
Air Density (g/ml)					
Water Density (g/ml)					
Density of the mass pieces (g/ml)					
Coefficient of expansion from the pycnometer material (°C^{-1})					
Water temperature (ºC)					
Other					

Random uncertainty (ml)		Systematic uncertainty (ml)	
Combined uncertainty (ml)		Expanded uncertainty (ml) (k=2)	

Comments:

Signature:

Annex 2 – Equipment

Balance

Laboratory	Type	Range (g)	Resolution (g)
IPQ	Mettler, PK 300	0 - 300	0,0001
CMI	Mettler-Toledo, AT400/A	0,01 – 405	0,0001
BNM-LNE	Mettler, AT400	0 – 405	0,0001
FORCE	Mettler-Toledo, AX205	80 / 221	0,00001 / 0,0001
PTB	Sartorious, ME414S	maximum loading 410	0,0001
NMi-VSL	Mettler, PK300	0 – 300	0,0001
SLM	Analytical, AG 204	205	0,0001
UME	Mettler-Toledo, AT400	0 - 405	0,0001
CEM	Mettler, AX-205	220	0,00001
IMGC	Electronic, Mettler AT400	400	0,00001
OMH	Mettler, AX1004	0 – 1109	0,0001
EIM	Mettler, PM 400	0 – 410	0,001
BEV	Precisa, 240 A	max. 244	0,0001
SP	Mettler, AT	200	0,00001

Water thermometer

Laboratory	Type	Range (°C)	Resolution (°C)
IPQ	Digital	-30 to +150	0,1
CMI	Mercury	0 to 30	0,1
BNM-LNE	Pt100 HP34420	0 to 40	0,001
FORCE	Goldbrand, Hg	0 to 50	0,1
PTB	25W-platinum-resistance (PRT) ROSEMOUNT 162CE and resistance measuring bridge PAAR MKT -25	-40 to +157	0,001
NMi-VSL	Prema 4001 Digital multimeter including 3 NTC elements	-20 to +80	0,0001 kΩ
SLM	Glass, laboratory	18 to 35	0,05
UME	Guildline/9540	-40 to +180	0,001
CEM	Labfacility/Tempmaster 100	18 to 24	0,001
IMGC	Hart Scientific 1560	0 to 100	0,001
OMH	Hewlett Packard 2801A	0 to 30	0,001
EIM	Pt-100, S/N: 3	-50 to +420	0,01
BEV	Liquid in Glass	17,8 to 22,2	0,01
SP	Uni-system U241	-45 to 198	0,001

Air thermometer

Laboratory	Type	Range (°C)	Resolution (°C)
IPQ	Digital	0 to 50	0,1
CMI	Electronic, COMMETER THPZ	0 to 40	0,1
BNM-LNE	Pt100 - AOIP IT20	0 to 40	0,02
FORCE	Goldbrand, Hg	0 to 50	0,1
PTB	SCHNEIDER Hg	18 to 26	0,05
NMi-VSL	Prema 4001 Digital multimeter including 3 NTC elements	-20 to +80	0,01
SLM	Glass	0 to 50	0,1
UME	Vaisala 38 E	-40 to +80	0,01
CEM	ASL/F250+SB250	18 to 24	0,001
IMGC	Pt100	-	0,01
OMH	Testo 601	0 to 70	0,1
EIM	Rotronic	-20 to +60	0,1
BEV	Opus 10	-20 to +50	0,1
SP	Testotherm 610	-20 to +70	0,1

Barometer

Laboratory	Type	Range (hPa)	Resolution (hPa)
IPQ	Digital	800 - 1150	0,1
CMI	Electronic COMMETER THPZ	950 – 1100	1
BNM-LNE	VAISALA PTB220	500 – 1100	0,01
FORCE	Präzisions Aneriod	870 – 1050	1
PTB	DRUCK MESSTECHNIK DPI141	950 – 1050	0,01
NMi-VSL	Druck DPI 145	800 – 1150	0,01
SLM	Hg	800 – 1100	1
UME	DESGRANGES & HUAT DPM1	0 – 1600	0,001
CEM	Druck/DPI-141	800 – 1200	0,01
IMGC	Ruska	0 – 1300	0,01
OMH	Wallace-Tiernan Diptron 3 plus	0 – 1100	0,1
EIM	Lufft precision analog	870 - 1050	0,5
BEV	Paroscientific mod. 740-16B	750 – 1150	0,001
SP	Paulin Linod	925 – 1055	0,1

Hygrometer

Laboratory	Type	Range (%)	Resolution (%)
IPQ	Digital	0 - 100	0,1
CMI	Electronic, COMMETER THPZ	5 - 95	1
BNM-LNE	VAISALA HMB230	0 - 100	0,1
FORCE	Termohydrograph	0 - 100	5
PTB	VAISALA HMI36 with HMI35B-sensor	30 - 75	0,1
NMi-VSL	Novasina MS1	20 - 80	0,1
SLM UME	Hair-type Vaisala 38 E	5 - 100 (0 - 100	2 0,01
CEM	MBW/DP3-D-SH-I	(1 to 15) ºC	100 mK
IMGC	General Eastern	0 - 100	0,1
OMH	Testo 601	0 - 100	0,1
EIM	Rotronic	0 - 100	0,1
BEV	Opus 10	10 - 95	0,1
SP	Testotherm 610	0-100	0,1

Annex 3 – Degrees of equivalence between laboratories of the EUROMET comparison in nl (ml ×10^{-6})

	IPQ		CMI		BNM-LNE		FORCE		PTB		NMi-VSL	
	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
IPQ			-39	61	7	28	1	103	-14	27	9	65
CMI	39	61			46	58	40	115	25	57	48	82
BNM-LNE	-7	28	-46	58			-6	101	-21	18	2	62
FORCE	-1	103	-40	115	6	101			-15	101	8	117
PTB	14	27	-25	57	21	18	15	101			23	61
NMi-VSL	-9	65	-48	82	-2	62	-8	117	-23	61		
UME	-19	89	-58	103	-12	87	-18	132	-33	87	-10	105
CEM	-11	29	-50	59	-4	22	-10	101	-25	21	-2	62
IMGC	-5	34	-44	61	2	28	-4	103	-19	27	4	65
OMH	13	29	-26	58	20	21	14	101	-1	20	22	62
EIM	-100	155	-139	163	-93	154	-99	183	-114	154	-91	165
BEV	-10	48	-49	69	-3	43	-9	108	-24	43	-1	73
SP	-3	82	-42	96	4	79	-2	127	-17	79	6	98

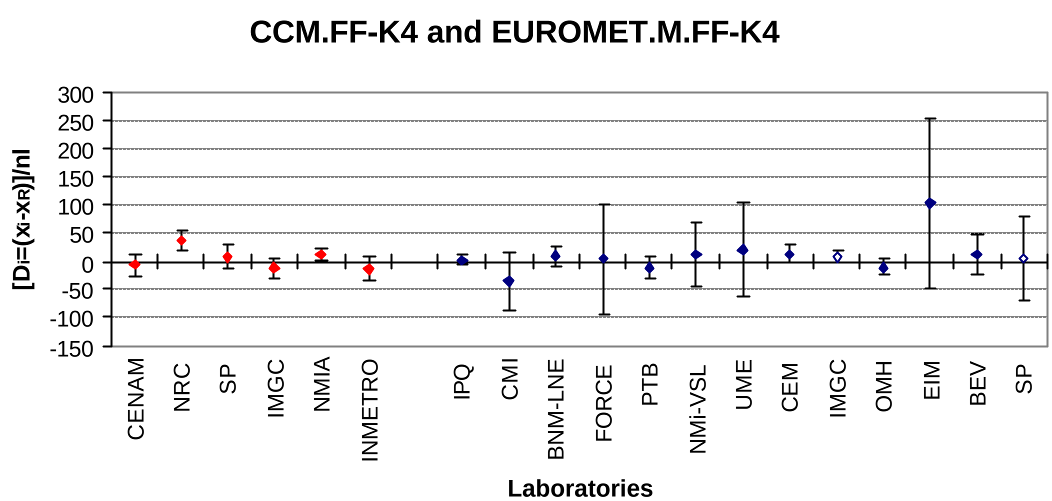
	UME		CEM		IMGC		OMH		EIM		BEV		SP	
	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
IPQ	19	89	11	29	5	34	-13	29	100	155	10	48	0	82
CMI	58	103	50	59	44	61	26	58	139	163	49	69	4	96
BNM-LNE	12	87	4	22	-2	28	-20	21	93	154	3	43	0	79
FORCE	18	132	10	101	4	103	-14	101	99	183	9	108	0	127
PTB	33	87	25	21	19	27	1	20	114	154	24	43	2	79
NMi-VSL	10	105	2	62	-4	65	-22	62	91	165	1	73	-1	98
UME			-8	88	-14	89	-32	87	81	176	-9	95	-2	116
CEM	8	88			-6	29	-24	23	89	155	-1	44	-1	80
IMGC	14	89	6	29			-18	29	95	155	5	48	0	82
OMH	32	87	24	23	18	29			113	154	23	44	2	80
EIM	-81	176	-89	155	-95	155	-113	154			-90	159	-10	172
BEV	9	95	1	44	-5	48	-23	44	90	159			-1	88
SP	16	116	8	80	2	82	-16	80	97	172	7	88		

Annex 4 – Degrees of equivalence between each laboratory participating in EUROMET comparison and each laboratory participating in CCM.FF-K4, in nl

	CENAM		NRC		SP		IMGC		NMIA		INMETRO	
	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
IPQ	10	21	-33	21	-5	23	15	20	-10	14	16	23
CMI	-29	55	-72	55	-44	55	-24	54	-49	53	-23	56
BNM-LNE	17	25	-26	25	2	27	22	25	-3	20	23	27
FORCE	11	99	-32	99	-4	100	16	99	-9	98	17	100
PTB	-4	26	-47	26	-19	28	1	26	-24	21	2	28
NMi-VSL	19	59	-24	59	4	60	24	59	-1	57	25	60
UME	29	85	-14	85	14	86	34	85	9	84	35	86
CEM	21	24	-22	23	6	25	26	23	1	18	27	25
IMGC	15	21	-28	21	0	23	20	20	-5	14	21	23
OMH	-3	24	-46	24	-18	26	2	23	-23	19	3	26
EIM	110	153	67	153	95	153	115	153	90	152	116	153
BEV	20	39	-23	39	5	40	25	39	0	36	26	40
SP	13	77	-30	77	-2	78	18	77	-7	76	19	78

Annex 5 – Degrees of equivalence of each laboratory of EUROMET comparison with respect to the reference value determined in CCM.FF-K4 for the Pycnometer nº TS 03.04.03

Lab.	$D_i(x_i - x_R)$ (nl)	U_i (nl)
IPQ	3	9
CMI	-37	51
BNM-LNE	9	17
FORCE	3	98
PTB	-11	19
NMi-VSL	12	56
UME	22	83
CEM	14	14
IMGC	8	9
OMH	-10	15
EIM	103	152
BEV	13	35
SP	6	75



Red diamonds: CCM.FF-K4 participating laboratories
Blue diamonds: EUROMET-K4 participating laboratories
Unfilled blue diamonds : Linking laboratories

Annex 6 – Uncertainty components for each laboratory

IPQ-1

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty c_i x $u(x_i)$
Mass (g)	Normal	7,43E-05	1,00E+00	7,43E-05
Density of the mass pieces (g/ml)	Normal	1,15E-01	1,85E-03	2,14E-04
Water density (g/ml)	Rectangular	1,19E-05	-1,00E+02	1,19E-03
Air density (g/ml)	Rectangular	2,89E-07	8,78E+01	2,53E-05
Coefficient of expansion from the pycnometer material (°C^{-1})	Rectangular	2,89E-07	-1,00E+01	2,89E-06
Water temperature (ºC)	Normal	5,00E-02	-1,00E-03	5,00E-05

CMI

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty c_ix $u(x_i)$
Mass filled (g)	normal	3,496E-04	1,003E+00	3,507E-04
Mass empty (g)	normal	3,496E-04	-1,003E+00	3,507E-04
Air Density (g/ml)	normal	5,000E-06	8,589E+01	4,295E-04
Water Density (g/ml)	normal	2,628E-05	-1,003E+02	2,636E-03
Density of the mass pieces (g/ml)	uniform	1,155E-01	1,805E-03	2,084E-04
Coefficient of expansion from the pycnometer material (°C^{-1})	uniform	5,774E-07	-1,830E+02	1,056E-04
Water temperature (ºC)	normal	1,282E-01	-9,998E-04	1,282E-04

BNM-LNE

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty $c_i \times u(x_i)$
Weighing empty (g) Weighing filled (g)	rectangle rectangle	0,000 23 0,000 34	1,000 1,000	0,000 23 0,000 34
Air Density (g/ml)	rectangle	1,00E-06	48,2	0,000 05
Water Density (g/ml)	rectangle	4,2E-07	100,0	0,000 04
Density of the mass pieces (g/ml)	included in empty and dry weghings			
Coefficient of expansion from the pycnometer material (°C^{-1})	rectangle	1,00E-06	0,1	0,000 00
Water temperature (ºC)	rectangle	0,02	0,02	0,000 41
Pycnometer temperature (ºC)	rectangle	0,02	0,001	0,000 02

FORCE

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty $c_i \times u(x_i)$
Mass (g)	1	0,0023	1,003	0,0023069
Air Density (g/ml)	0,58	0,0029	0,1	0,00029
Water Density (g/ml)	0,58	0,0058	0,1	0,0041
Density of the mass pieces (g/ml)	(included in Mass)			
Coefficient of expansion from the pycnometer material (°C^{-1})	0,58	0,00000116	124,6	0,000144536
Water temperature (ºC)	0,58	0,203	0,02	0,00035
Other	0,58	0,0000058	120	0,000696

PTB-1

Quantity (xi)	Standard Uncertainty $u(x_i)$	Sensitivity Coefficient c_i	Uncertainty c_i x $u(x_i)$
Weighing value (1st weighing of the empty pycnometer)	32,0E-6 g	-1,0	-32E-6
Weighing value (2nd weighing of the filled pycnometer)	41,0E-6 g	1.0	41E-6
Air density (1st weighing of the empty pycnometer)	990E-9 g·cm^{-3}	110	110E-6
Air density (2nd weighing of the filled pycnometer)	990E-9 g·cm^{-3}	-18	-18E-6
Water density	5,60E-6 g·cm^{-3}	-100	-560E-6
Volume expansion coefficient of the pycnometer glass material	1,15E-6 K^{-1}	0,20	230E-9
Water temperature	0,0120 °C	-1,0E-3	-12E-6
Correction to consider the accuracy of the adjustment of the in filled water at the top of the stopper	80,8E-6 cm^3	1,0	81E-6
Correction to consider the accuracy of the stopper height position in the pycnometer flask	173E-6 cm^3	1,0	170E-6
Correction to consider the difference between the temperature of the water in filled in the bore and the temperature of the water in the pycnometer flask	7,16E-6 cm^3	1,0	7,2E-6
Correction to consider the difference between the temperature of the bore and the temperature of the pycnometer flask	346E-9 cm^3	1.0	350E-9
Correction to consider a water skin on the outer surface of the pycnometer after thermosetting, removing out of the bath and drying	173E-6 cm^3	1.0	170E-6

IPQ-2

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty $c_i \times u(x_i)$
Mass (g)	Normal	7,41E-05	1,00E+00	7,43E-05
Density of the mass pieces (g/ml)	Normal	1,15E-01	1,88E-03	2,17E-04
Water density (g/ml)	Rectangular	1,17E-05	-1,00E+02	1,18E-03
Air density (g/ml)	Rectangular	2,89E-07	8,79E+01	2,54E-05
Coefficient of expansion from the pycnometer material (°C^{-1})	Rectangular	2,89E-07	-3,00E+01	8,67E-06
Water temperature (ºC)	Normal	5,23E-02	-1,00E-03	5,23E-05

PTB-2

Quantity (xi)	Standard Uncertainty $u(x_i)$	Sensitivity Coefficient c_i	Uncertainty $c_i \times u(x_i)$
Weighing value (1st weighing of the empty pycnometer)	25,0E-6 g	-1,0	-25E-6
Weighing value (2nd weighing of the filled pycnometer)	36,0E-6 g	1,0	36E-6
Air density (1st weighing of the empty pycnometer)	1,00E-6 $g \cdot cm^{-3}$	110	110E-6
Air density (2nd weighing of the filled pycnometer)	1,00E-6 $g \cdot cm^{-3}$	-18	-18E-6
Water density	5,60E-6 $g \cdot cm^{-3}$	-100	-560E-6
Conventional density of the weights used for substitution			
Volume expansion coefficient of the pycnometer glass material	1,15E-6 K^{-1}	0.10	120E-9
Water temperature	0,0120 °C	-1,0E-3	-12E-6
Correction to consider the accuracy of the adjustment of the in filled water at the top of the stopper	80,8E-6 cm^3	1,0	81E-6
Correction to consider the accuracy of the stopper height position in the pycnometer flask	173E-6 cm^3	1,0	170E-6
Correction to consider the difference between the temperature of the water in filled in the bore and the temperature of the water in the pycnometer flask	7,16E-6 cm^3	1,0	7,2E-6
Correction to consider the difference between the temperature of the bore and the temperature of the pycnometer flask	346E-9 cm^3	1,0	350E-9
Correction to consider a water skin on the outer surface of the pycnometer after thermosetting, removing out of the bath and drying	173E-6 cm^3	1,0	170E-6

NMi-VSL

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty $c_i \times u(x_i)$
Mass (g)	normal	1,30E-03	1,00E+00	1,31E-03
Air Density (g/ml)	normal	1,37E-06	8,79E+01	1,20E-04
Water Density (g/ml)	normal	2,48E-05	-1,00E+02	2,49E-03
Density of the mass pieces (g/ml)	normal	7,00E-03	1,86E-03	1,30E-05
Coefficient of expansion from the pycnometer material (°C^{-1})	normal	1,00E-06	1,37E+02	1,37E-04
Water temperature (°C)	normal	9,00E-02	1,00E-03	9,01E-05
Other wipe off	normal	1,00E-03	1,00E+00	1,00E-03

SLM

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty $c_i \times u(x_i)$
Mass (g)	normal	8,00E-05	1	0,000080
Air Density (g/ml)	rectangular	1,04E-05	87,5	0,000909
Water Density (g/ml)	rectangular	2,02E-05	100	0,002021
Density of the mass pieces (g/ml)	rectangular	2,31E-02	0,00188	0,000043
Coefficient of expansion from the pycnometer material (°C^{-1})	rectangular	1,15E-06	181	0,000209
Water temperature (°C)	rectangular	7,51E-02	0,001	0,000075
Other - meniscus reading - cm	triangular	8,16E-03	0,0126	0,000103

UME

Quantity (x_i)	**Distribution**	**Standard uncertainty $u(x_i)$**	**Sensitivity coefficient c_i**	**Uncertainty c_i x $u(x_i)$**
Mass (g)	Normal	0,0035644	1,0030007	0,0035751
Air Density (g/ml)	Normal	0,0000006	87,8959233	0,0000540
Water Density (g/ml)	Normal	0,0000215	100,4094534	0,0021610
Density of the mass pieces (g/ml)	Normal	0,0480000	0,0018353	0,0000881
Coefficient of expansion from the pycnometer material (°C^{-1})	Normal	0,0000033	83,4600467	0,0002782
Water temperature (ºC)	Normal	0,1657664	0,0010009	0,0001659

CEM

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty c_i x $u(x_i)$
Empty mass W1	normal	8,78E-05	-1003	0,0881
Full mass W2	normal	2,90E-04	1003	0,2909
Evaporated mass Wevap	normal	5,37E-04	1003	0,5386
Water Temperature	normal	0,015	21	0,3150
Water Air saturation	rectangular	0,116	-0,25	0,0290
Water Density Equation error	rectangular	4,15E-04	-101	0,0419
Air Temperature	rectangular	0,094	-0,36	0,0338
Air Pressure	normal	3,8	0,0010	0,0038
Air Relative Humidity	rectangular	0,0045	-0,93	0,0042
CO_2 molar fraction	rectangular	5,80E-05	40	0,0023
Air Density Equation relative error	rectangular	1,03E-04	98	0,0101
Cubic expansion coefficient for the pycnometer material	rectangular	2,90E-08	1101	0,00003
Pycnometer material Temperature	normal	0,015	-0,99	0,0149
Density of the mass calibration weights	rectangular	15	0,0018	0,0270

IMGC

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty $c_i \times u(x_i)$
Mass (g) Air Density (g/ml)	Gaussian Rectangular	0,00039 0,000003	1,002893 87,883366	0,00039 0,00026
Water Density (g/ml)	Rectangular	0,000003	-100,396721	0,00030
Density of the mass pieces (g/ml)	Rectangular	0,173	0,001829	0,00032
Coefficient of expansion from the pycnometer material (°C^{-1}) Water temperature (ºC)	Rectangular Rectangular	0,0000012 0,046	-31,849442 0,020051	0,00004 0,00093

OMH

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty $c_i \times u(x_i)$
Mass (g)	normal	0,000073	1,002837	0,000073
Air Density (g/ml)	rectangular	0,000001	87,663	0,000088
Water Density (g/ml)	normal	0,0000025	100,3894	0,000251
Density of the mass pieces (g/ml)	normal	0,005	0,0019062	0,00001
Coefficient of expansion from the pycnometer material (°C^{-1})	rectangular	0,000001	0,6005	0,000001
Water temperature (ºC)	normal	0,003	0,0010009	0,000003

EIM

Quantity (x_i)	Standard Uncertainty $u(x_i)$	Sensitivity Coefficient c_i	Uncertainty ci x u(xi)
Mass of weights equal to empty standard (g)	9,25E-05	-1,003425	-9,282E-05
Mass of weights equal to filled standard (g)	0,000188	1,003425	1,886E-04
Air Density (g/ml)	4,25E-07	8,78E+01	3,733E-05
Water Density (g/ml)	2,60E-05	-1,00E+02	-2,610E-03
Density of the mass pieces (g/ml)	0,07	1,88E-03	1,317E-04
Coefficient of expansion of the pycnometer material (°C^{-1})	5,00E-07	-272,279	-1,361E-04
Water temperature (°C)	5,00E-02	-1,00E-03	-5,005E-05
Mass difference between weights and filled standard (g)	5,40E-03	1,00E+00	5,422E-03
Mass difference between weights and empty standard (g)	2,57E-03	-1,003575	-2,578E-03

BEV

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty c_i x $u(x_i)$
Mass (g) m2	Type A	1,00E-03	1,00E-03	0,001
m1	Type A	3,00E-04	-1,00E-03	0,0003
Air Density (g/ml)	rectangular	2,30E-03	8,70E-08	0,0002
Water Density (g/ml)	rectangular	0,0145	-1,00E-07	0,0014
Density of the mass pieces (g/ml)	rectangular	144	-5,90E-14	0,0000086
Coefficient of expansion from the pycnometer material (°C^{-1})	rectangular	1,15E-06	-7,00E-07	0,00000089
Water temperature (ºC)	rectangular	0,0115	-1,00E-09	0,000012
Other	rectangular	577e-12 m3	1	0,00058

SP

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty c_i x $u(x_i)$
Level adjustment	triangular	2,04E-01	7,85E-10	1,61E-04
Water temperature on water density	triangular	1,22E-01	2,30E-08	2,82E-03
Temperature pycnometer	triangular	1,22E-01	1,00E-09	1,22E-04
Water density (at given temp.)	rectangular	1,15E-02	1,00E-07	1,15E-03
Mass in control weights filled Pyc.	normal	4,74E-07	1,00E-03	2,37E-04
Air density	rectangular	1,44E-03	8,80E-08	1,27E-04
Mass pycnometer	triangular	4,25E-07	1,00E-02	2,01E-03
Volume expansion coefficient	rectangular	5,77E-07	1,79E-04	1,04E-04
Balance, excetricity, linearity, rep.	rectangular	5,00E-08	1,00E-04	2,89E-06
Reading filled standard	rectangular	2,89E-01	1,00E-11	2,89E-06
Reading corresponding mass standard	rectangular	2,89E-01	1,00E-11	2,89E-06
Resolution balance	rectangular	5,77E-11	1,00E-01	5,77E-06
Static electricity	rectangular	2,31E+02	1,00E-11	1,16E-03

IPQ-3

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty c_i x $u(x_i)$
Mass (g)	Normal	7,41E-05	1,00E+00	7,43E-05
Density of the mass pieces (g/ml)	Normal	1,15E-01	1,85E-03	2,13E-04
Water density (g/ml)	Rectangular	1,22E-05	-1,00E+02	1,22E-03
Air density (g/ml)	Rectangular	2,89E-07	8,79E+01	2,54E-05
Coefficient of expansion from the pycnometer material (°C^{-1})	Rectangular	2,89E-07	-4,00E+01	1,16E-05
Water temperature (ºC)	Normal	5,26E-02	-1,00E-03	5,26E-05