Instituto Português da Qualidade

Portuguese Institute for Quality

Final Report

Bilateral comparison of a 100ml Gay-Lussac Pycnometer

EUROMET Project no. 793

IPQ – Coordinator of the comparison

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Contents

1. Introduction

During the EUROMET meeting on April 2004, the Bulgarian National Metrological Institute (NCM) manifested the interest to participate in a bilateral comparison with the Portuguese NMI, IPQ.

The main purpose of this project is to compare the results and uncertainties of a volume calibration of a glass 100 ml Gay-Lussac Pycnometer. This project has a similar protocol as the EUROMET project nº 692 and allows to link the NCM results to the participating countries of the project 692 because the standard pycnometer is the same, nº 144.

1.1. Participants

Table 1 - Participants in the EUROMET project 793

Country	Laboratory	Responsible	Contact
Portugal	IPQ	Elsa Batista	Tel: +35 1212948167 e-mail: ebatista@mail.ipq.pt
Bulgaria	NCM	Nadja Vladimirova	Tel: +395 2 722 081 e-mail: ncm@sasm.orbitel.bg

1.2. Schedule

Table 2 – Time schedule

Country	Laboratory	Periods
Portugal	IPQ	July 2004
Bulgaria	NCM	September 2004
Portugal	IPQ	November 2004

2. The instrument

The used instrument is the same as for the EUROMET project 692, a 100 ml Gay-Lussac pycnometer of borosilicate glass (see figure 1), with a coefficient of thermal expansion of $10\times10^{-6}\ C^{-1}$ and is normally used for the measurement of the liquids density[(1)].

Figure 1- Pycnometer nº 144

3. The suggest method

The suggest method to perform the pycnometer calibration was the gravimetric one. The following formula described in ISO 4787(2) can be used for the calculation of the contained volume:

$$V_{20} = (m_2 - m_1) \times \frac{1}{\rho_W - \rho_A} \times \left(1 - \frac{\rho_A}{\rho_B}\right) \times \left[1 - \gamma(t - 20)\right] \tag{1}$$

4. The experimental procedure

The following experimental procedure was proposed:

- Weigh the empty pycnometer and record the mass m_1.
- Fill the pycnometer with water, taking care to avoid the creation of air bubbles.
- Place the stopper of the pycnometer firmly in position and wipe off any excess liquid from the outside of the pycnometer.
- Weigh the filled pycnometer recording the mass m_2.
- For comparable results perform 10 measurements under repeatability conditions.

The results were given for a temperature of 20 ºC.

4.1. Equipment

Each laboratory described the equipment used in the calibration and the respective traceability.

Table 3 – Equipment characteristics

Balance	**Type**	**Range**	**Resolution**
IPQ	Electronic	(0 - 300) g	0,0001 g
NCM	Electronic	Max 500g	0,0001 g
Water thermometer	**Type**	**Range**	**Resolution**
IPQ	Digital	(-30 to +150) ºC	0,1 ºC
NCM	Digital	(-200 to +850) ºC	0,01 ºC
Air thermometer	**Type**	**Range**	**Resolution**
IPQ	Digital	(0 to +50) ºC	0,1 ºC
NCM	Digital	(-200 to +850) ºC	0,01 ºC
Barometer	**Type**	**Range**	**Resolution**
IPQ	Digital	(800- 1150) hPa	0,1 hPa
NCM	Mercury	(570- 1090) hPa	0,05 hPa
Hygrometer	**Type**	**Range**	**Resolution**
IPQ	Digital	(0 - 100) %	0,1 %
NCM	Hair	(0 - 100) %	5 %

4.2. Type of water

The water should have the quality suitable for the purpose of the 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	Spieweck	2,614
NCM	Distilled	Tanaka	2

Both participants used at least distilled water; the conductivity values are all according to the ISO 3696[(3)] < 5μS/cm.

4.3. Mass standards

Some information about the type of mass standard used was also requested:

Table 5 – Mass characteristics

Laboratory	Type	Density (g/cm^3)
IPQ	E2	8,01
NCM	F1	8,00

4.4. Cleaning

Also the way of cleaning the standard was different in each laboratory according to the table 6.

Table 6 – Cleaning the standard

Laboratory	Cleaning Procedure	Mass empty of the pycnometer (g)
IPQ	Cleaning with water and drying with dry air	42,5229
NCM	Cleaning with dishwashing agent then distilled water; in drying chamber	42,5235

5. Experimental conditions

Both participants described the ambient conditions.

Table 7 - Ambient conditions

Laboratory	Air Temperature (ºC)	Pressure (hPa)	Humidity (%)	Air density (g/cm^3)	Water Temperature (ºC)
IPQ-1	19,8	1016,4	46,9	0,00120	19,7
NCM	20,74	954,61	58,8	0,00113	20,34
IPQ-2	20,5	1005,0	70,5	0,00119	20,4

6. Measurement results

6.1. Volume measurements results

Table 8 – Volume results

Laboratory	Volume (ml)	Uncertainty (ml) with *k*=2
IPQ-1	100,0917	0,0025
NCM	100,0928	0,0024
IPQ-2	100,0915	0,0024

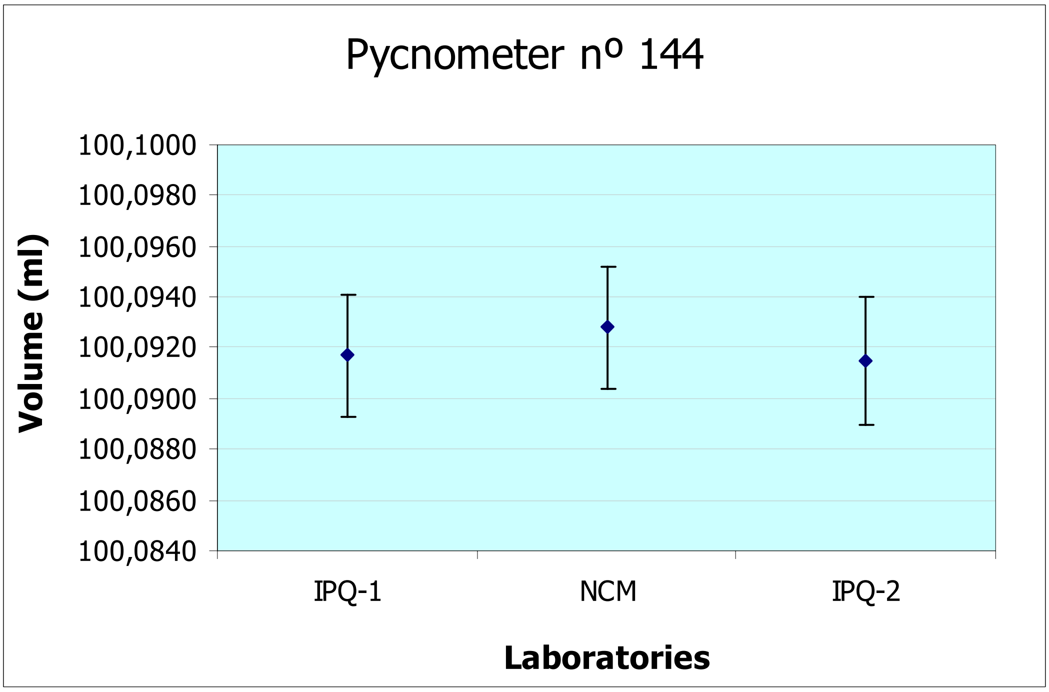

Figure 2 – Volume of Pycnometer nº 144

6.2. Determination of the weighted mean

The weighted mean and associated uncertainty of the three presented results were calculated according to the following formulas[(4)]:

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

$$u(y) = \sqrt{\frac{1}{1/u^2(x_1) + \ldots + 1/u^2(x_n)}} \qquad (3)$$

The determined values are ***y* = 100,0920 ml, *u(y)* = 0,0014 ml with *k*=2**

In the figure 4 it is shown the measurement results with the weighted mean and associated uncertainty.

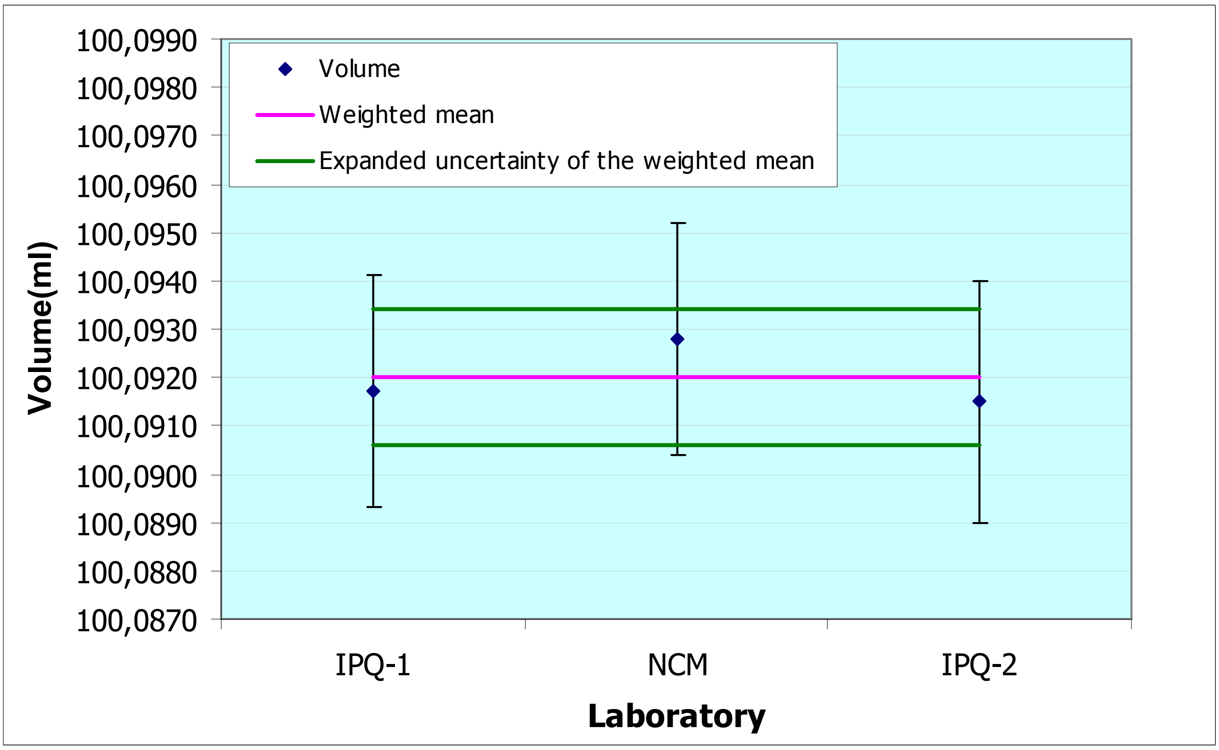

Figure 3 – Participant results compared with weighted mean

From this figure it can be observed that the volume results are quite close to each other and consistent with the weighted mean.

6.3. The reference value

In order to link the NCM results to the participating countries of the EUROMET project 692 its necessary to compare the determined reference value of this project to the presented volume measurement results.

The reference value determined for the EUROMET project 692 is, y_{ref} **= 100,0914 ml,** and the associated uncertainty, $u(y_{ref})$ **= 0,0006 ml with** k**=2**. These values were calculated according to the formula 2 and 3.

The following figure shows the relation between the reference value and the presented volumes.

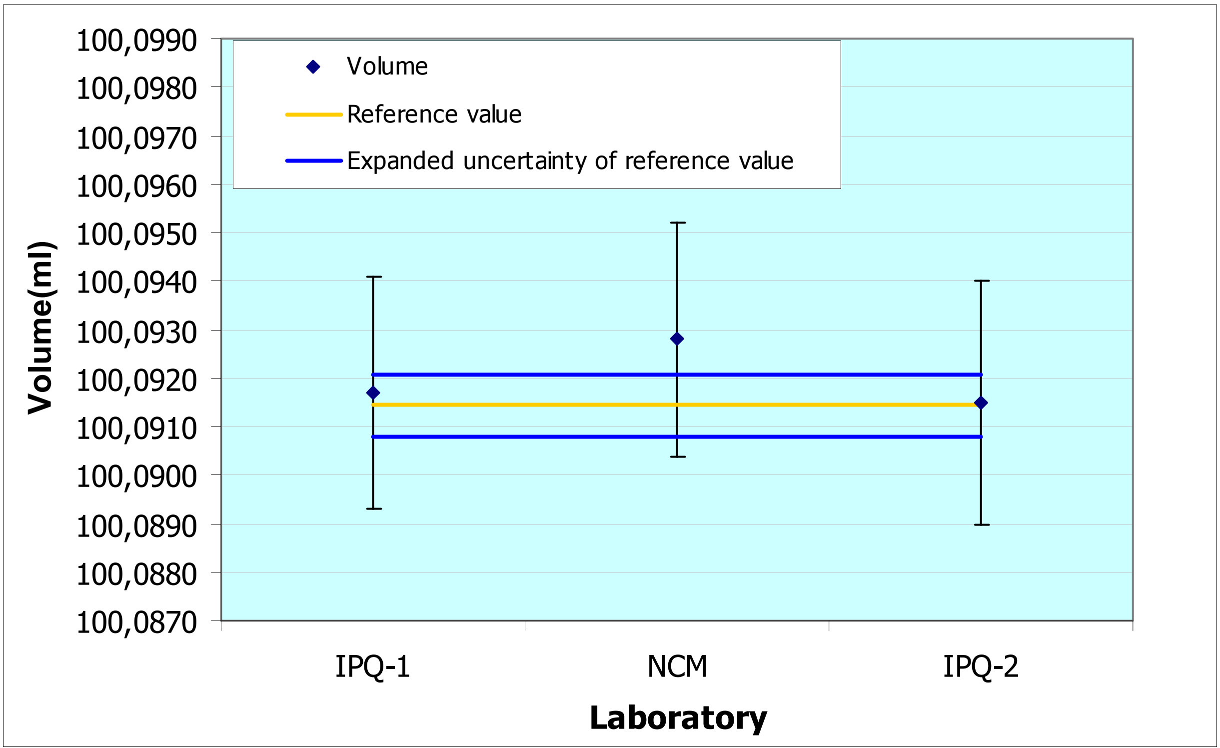

Figure 4 – Participant results compared with reference value determined in EUROMET project 692

The results are quite good; all three volume measurements are quite consistent with the reference value.

6.4. Degrees of equivalence

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

$$d_i = x_I - x_{ref} \qquad (4)$$

and $$U(d_i) = 2u(d_i) \qquad (5)$$

were $u(d_i)$ is given by

$$u^2(d_i) = u^2(x_i) - u^2(x_{ref}) \qquad (6)$$

The factor 2 in (5) gives 95% coverage under the assumption of normality.

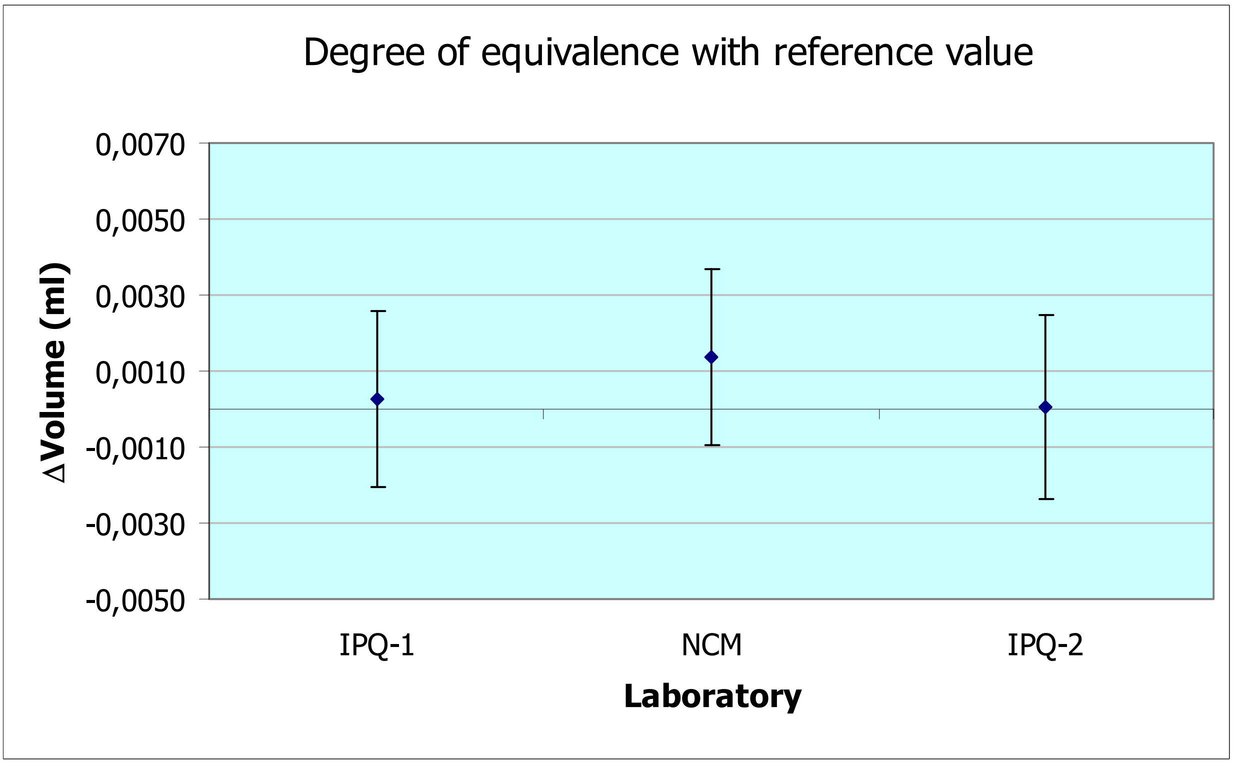

Figure 5 – Degree of equivalence between the laboratory and the reference value

The degree of equivalence between the laboratories and the reference is quite good.

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

$d_{i,j} = x_i - x_j$ (7)

$U(d_{i,j}) = 2u(d_{i,j})$ (8)

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

$u^2(d_{i,j}) = u^2(x_i) + u^2(x_j)$ (9)

The results are presented in table 9. The uncertainty is with a coverage factor of $k = 2$ presented in the lower part of the matrix.

Table 9 – Degree of equivalence between the laboratories

NMI	**IPQ-1**	**NCM**	**IPQ-2**	d_i **(ml)**
IPQ-1		0,0011	-0,0002	**0,0003**
NCM	0,0034		-0,0013	**0,0014**
IPQ-2	0,0035	0,0035		**0,0001**
$U(d_i)$ **(ml)**	**0,0023**	**0,0023**	**0,0024**	

In this table we can have a general idea of the differences in the volume results between the laboratories, which are very small.

7. Uncertainty presentation

7.1. Type A and type B uncertainty

It was requested that participants present the systematic and random standard uncertainties.

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

Figure 6 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 %.

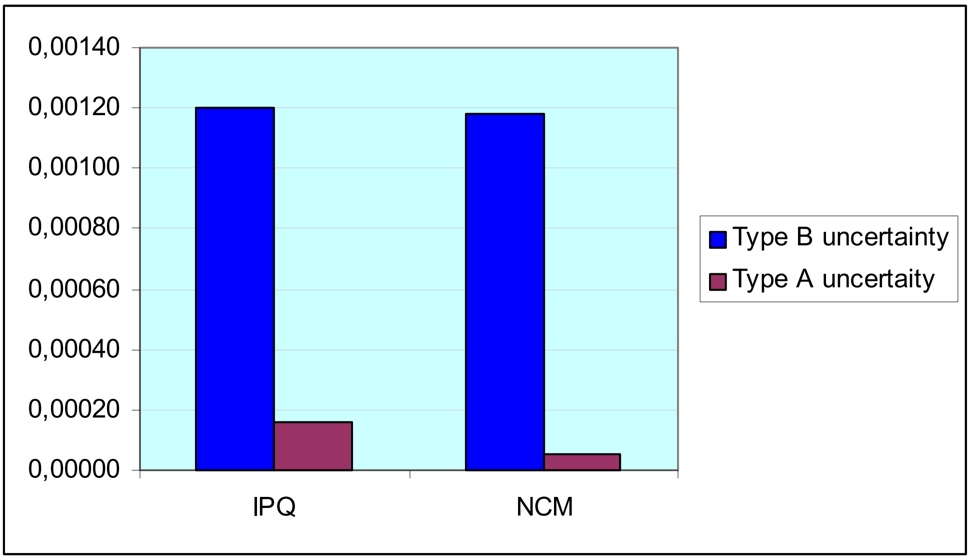

Figure 6 - Difference between the type A and type B uncertainty

7.2. Uncertainty components

A spreadsheet (Annex 1) with the proposed uncertainty components was presented to all participants.

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. The uncertainty results for IPQ-1 and IPQ-2 were merged because they are very similar.

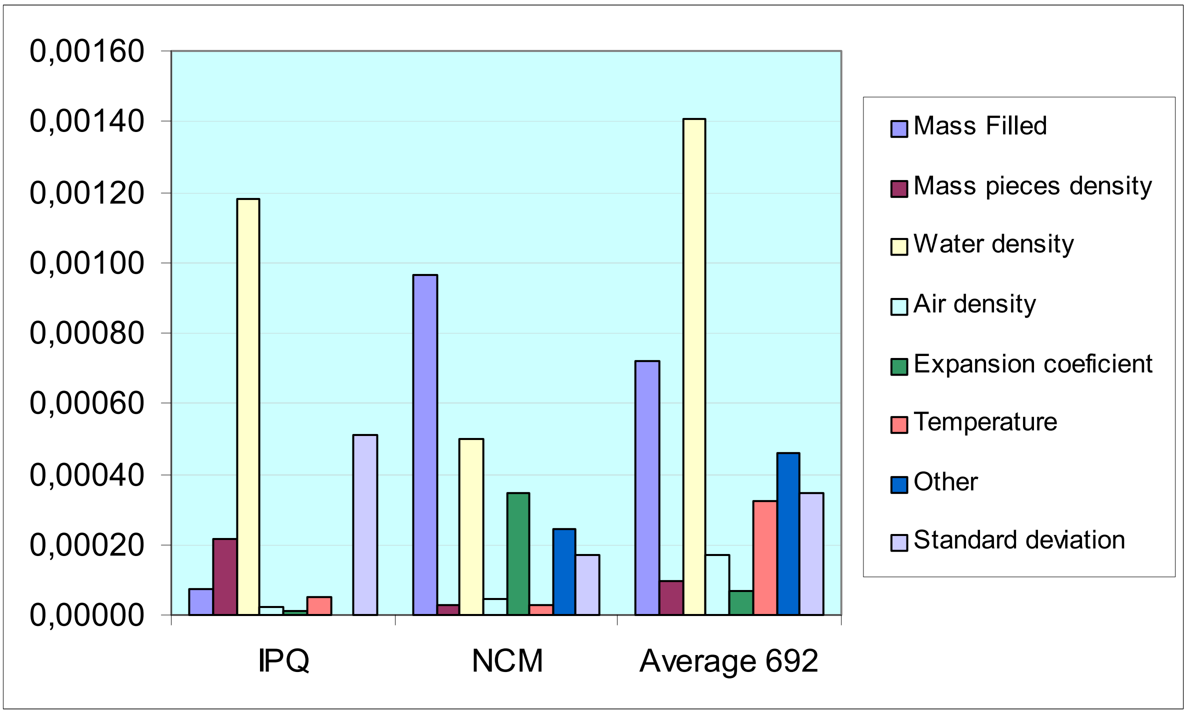

Figure 7 - Uncertainty components

As it can bee seen from the figure there are some significant differences in the stated uncertainty components values. For IPQ the larger source of uncertainty is the water density and for NCM the mass filled. This statements are according to the results presented in EUROMET project were the larger source is the water density but the second is the mass filled.

The uncertainty components for each laboratory are defined in greater detail in Annex 2.

8. Conclusions

This bilateral comparison involved IPQ and NCM, the used standard was the same as the one used for EUROMET 692, a 100 ml Gay Lussac Pycnometer, nº 144.

The volume results are quite similar and consistent with each other and with the determined reference value in Project EUROMET 692.

The uncertainty values of the determined volumes are also quite close between laboratories with some differences in the sated components uncertainty, for IPQ the most important component is the water density and for NMC is the mass filed, this statements are also in accordance with the results presented in the EUROMET project 692.

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

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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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<u>EUROMET Project "Volume calibration of 100 ml Gay-Lussac Pycnometer"</u>

Results form

Ambient Conditions

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

Measurement results

Test number	Instrument mass empty (g)	Instrument mass filled (g)	Water temperature (°C)	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 ν_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 (°C)					
Other					

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

Comments:

Signature:

Annex 2 – 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

NCM

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty c_i x $u(x_i)$
Mass (g)	Normal	4,81E-04	2,00572087	9,64E-04
Air Density (g/ml)	Normal	4,88E-07	87,8802334	-4,28E-05
Water Density (g/ml)	Rectangular	5,00E-06	-100,3936	-5,02E-04
Density of the mass pieces (g/ml)	Rectangular	1,73E-02	-0,0017603	-3,05E-05
Coefficient of expansion from the pycnometer material (°C^{-1})	Rectangular	5,77E-07	-34,432048	-3,44E-04
Water temperature (ºC)	Normal	3,11E-02	-0,0010009	-3,11E-05
Air bubles in the water, ml	Rectangular	-2,46E-06	-100,3936	0,0002465
Setting the water meniscus, ml	Rectangular	0	1	0

IPQ -2

Quantity (xi)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty $c_i \times u(x_i)$
Mass (g)	Normal	7,43E-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	5,00E-02	-1,00E-03	-5,00E-05