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EURAMET REGIONAL KEY COMPARISON VOLUME COMPARISON AT 20 L

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Abstract – The EURAMET Key comparison “Volume comparison at 20 L”, between fourteen National Metrology Institutes (NMIs), was performed with a gravimetric method procedure. This paper describes the data evaluation (determination of the reference value and a chi-square test) and uncertainty analysis of the results.

Keywords: uncertainty, gravimetry, volume

1. INTRODUCTION

In the sequence of CIPM Key comparisons concerning volume calibrations an interregional comparison CCM.FF-K4 was performed between December 2003 and March 2005 for volume standards of 20 L and 100 mL [1]. The corresponding regional part of this comparison within Europe was performed in 2006 for a 100 mL Gay-Lussac Pycnometer - EUROMET.M.FF-K4a (EUROMET project number 692). It was decided during the EUROMET meeting in Istanbul 2007 to also perform the regional part of this key comparison at 20 L, as EUROMET.M.FF-K4b.

The used technical protocol was an updated version of the original one for the CCM.FF-K4. This comparison was guided by IPQ/Portugal with SP/Sweden acting has the pilot laboratory having taken part in the interregional exercise. Fourteen countries decided to participate in this comparison.

Table 1. Participants in the EUROMET.M.FF-K4b.

NMI	Country	Responsible
CENAM	Mexico	Roberto Arias
SP	Sweden	Peter Lau
(JV)	Norway	Gunn Svendsen
NMi VSL	Netherlands	Erik Smits
SMU	Slovakia	Miroslava Benkova
MKEH	Hungary	Csaba Czibulka
PTB	Germany	Joerg Riedel
SZMDM	Serbia	Branislav Tanasic
UME	Turkey	Umit Akcadag
INRIM	Italy	Giorgio Cignolo
EIM	Greece	Zoe Metaxiotou
METAS	Switzerland	Hugo Bissig
BEV	Austria	Wilhelm Kolaczia
CMI	Czech Republic	Tomas Valenta
IPQ	Portugal	Elsa Batista

One of three 20 L pipettes, 710-04FyV used in the CCM.FF-K4, was readjusted by CENAM/Mexico, who initiated this Key-comparison and produced the transfer standard (TS) as the original pilot laboratory. The TS is owned by the Inter-American Metrology System (SIM).

The main purpose of this project was to compare the experimental results and uncertainty calculations in calibrating this 20 L pipette and linking the intra-regional European results with the results obtained in the previous inter-regional CIPM key comparison.

2. THE TRANSFER PACKAGE

The transfer standard (TS) consisted of the 20 L pipette in two halves, a digital thermometer with an installed sensor, accessories and fittings for assembling and disassembling the standard.

Fig. 1. 20 L pipette nº 710-04FyV.

The 20 L pipette, which is made of stainless steel, has been designed to:

- Minimize the contribution of the meniscus reading to the volume uncertainty,
- Provide a leak-free metal to metal seal between the two parts of the container,
- Minimize the risk of volume changes, and
- Keep the air/liquid interface as small as possible.

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These characteristics were intended to produce repeatable and reproducible volume measurements in the order of 0,005 %, or better.

3. EXPERIMENTAL PROCEDURE

All the participating NMIs applied a gravimetric method to determine the volume of water, using their own mathematical model. The participants differed in the water preparation and the applied density formula. The most common formula in gravimetric volume determination is described is ISO 4787 [2]:

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

4. RESULTS

5.1. Stability of the TS

SP acting as the pivot laboratory made a calibration of the TS in the beginning and at the end of the comparison. The first measurement result obtained was considered to be the official results of SP. Also CENAM as the pilot who supplied the artefact performed measurements before the start and after the end of the comparison in Europe. A main purpose was to determine a value after volume adjustment and follow up the stability over time. The results are presented in the following table:

Table 2. Stability of the TS.

NMI	Measurement	Date	Volume (mL)	Uncertainty (mL)	ΔV (mL)
SP	Initial	May 2007	20 002,44	0,49	0,15
	Final	June 2008	20 002,29	0,49	
CENAM	Initial	April 2007	20 002,39	0,65	0,03
	Final	July 2008	20 002,36	0,54	

The initial and final results obtained by both CENAM and SP are consistent with each other. The difference in measured volume is considerably smaller than the stated uncertainty. This demonstrates that the TS had a stable volume during the entire comparison.

5.2. Measurement results

The measurement results presented by each participant are collected in table 3.

5.3. Determination of the key comparison reference value - KCRV

To determine the reference value of this key comparison the weighted mean (2) was selected, using the inverses of the squares of the associated standard uncertainties as the weights [3], according to the instructions given by the BIPM:

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

The obtained KCRV for Europe is: 20 002,12 ml

Table 3. Volume measurement results.

NMI	Volume (mL)	Uncertainty (mL)
Lab1*	20 002,44	0,49
Lab2	20 002,87	0,80
Lab3	20 000,95	1,22
Lab4	20 002,47	0,58
Lab5	20 002,07	0,94
Lab6	20 001,72	0,40
Lab7	20 002,32	0,36
Lab8*	20 002,14	0,39
Lab9*	20 002,04	0,39
Lab10	20 002,05	0,68
Lab11	20 002,23	0,39
Lab12	20001,95	0,33
Lab13	20002,11	0,48
Lab14	20000,95	1,74

* These laboratories took part in the over regional inter-comparison.

5.4. Determination of the uncertainty of the reference value

To calculate the standard deviation *u(y)* associated with the volume *y* [3] equation (3) was used:

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

The obtained expanded uncertainty $U = 2 \times u(y)$ of the reference value is: 0,13 mL.

5.5. Consistency test of results - Chi-square test

To identify eventual inconsistent results a chi-square test can be applied to all *n* calibration results [3].

$$\chi^2_{obs}=\frac{(x_1-y)^2}{u^2(x_1)}+...+\frac{(x_n-y)^2}{u^2(x_n)} \qquad (4)$$

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

The consistency check is regarded as failed at a significance level α= 5% if:

$\Pr\{\chi^2(\nu) > \chi^2_{obs}\} < 0,05$

The expected test value of the chi-square distribution $\chi^2(\nu)$=22,36 (at ν=13 and α=5 %) is definitely larger than the observed value χ^2_{obs} = 18,98, therefore the results are considered consistence with each other from a statistical point of view.

All the measurement results, the reference value and its uncertainty are presented in the following figure 2:

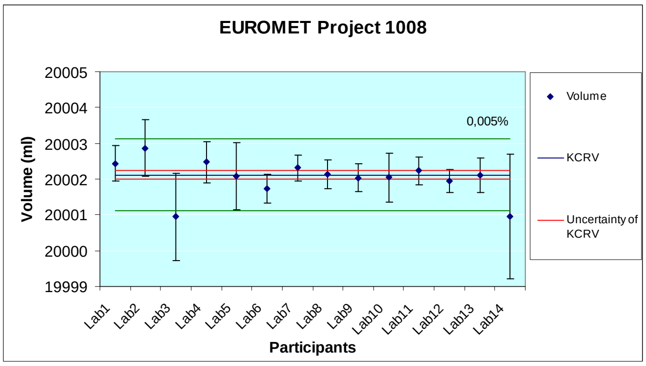

Fig. 2. Measurement results with reference value.

All the presented results overlapped the reference value with their respective uncertainty, which is quite good considering there were 14 participants.

5.6. Degree of equivalence

To calculate the degrees of equivalence between the KCRV and the laboratories the following formula is used [3]:

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

and $U(d_i) = 2 \times u(d_i)$ (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 equation (5) corresponds to a 95% coverage under the assumption of normality.

The results in figure 3 are given in relative terms (parts per million) together with the corresponding uncertainties. These are considerably smaller than those the participating laboratories claimed in their CMC tables (Calibration Measurement Capability). The main reason is the extraordinary inner surface of the TS that allows an almost complete emptying, which is rather unusual for normal vessels or proving tanks. Thus this exercise can be regarded as a verification of the laboratories CMC- claims.

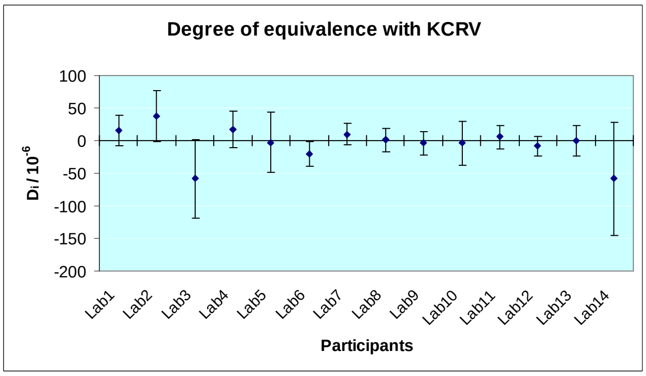

Fig. 3. Degree of equivalence with KCRV and corresponding uncertainty.

As shown in figure 3 all the D_i results cover the reference value considering their related uncertainty $U(D_i)$.

A degree of equivalence (DoE) can also be defined between any laboratory and all the others. A table of these results is not shown here. But the corresponding calculations refer to equation (8) to (10). There is a difference between equation (7) and (10). In the later one no correlation between the results from laboratories *i* and *j* is expected and thus both uncertainties are combined the usual way. In equation (7), however, the KCRV value is not independent from each result. In contrary there is a definite correlation of the KCRV to all results, which demands for a –sign making the uncertainty in the degree of equivalence smaller than the uncertainty in each stated result

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

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

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

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

The idea behind this construction is to show how the participating laboratories harmonize with each other. An optimal situation would be that those DoE were all less than the related uncertainties, which would mean all laboratories results would “overlap” all other laboratories’. But this can hardly be expected. In principle one could use the DoE to “translate” the calibration result from one laboratory to another. But as long as the DoE is within the uncertainty this is not a meaningful task and when it is outside it should be confirmed as a real bias before performing such a translation. Volume calibrations are performed pretty equally. A different situation may arise in flow calibrations or other comparisons due to different methods or equipment leading to a reproducible bias.

6. UNCERTAINTY PRESENTATION

6.1. Uncertainty components

It was requested that all participants present their uncertainty budget according to a spreadsheet supplied by the pilot laboratory and according to the GUM [4]. The suggested uncertainty components were the following:

- Balance
- Weights
- Water density
- Water temperature
- Ambient conditions
- Artefact
- Repeatability

The number of specified contributions by the laboratories varies from 5 to 15. Generally, however, only three of them really matter. With the exception of two or perhaps three laboratories having a somewhat larger value the remaining results are justifiably equivalent in size. An essential difference can lie in the used equipment. Some laboratories presented uncertainty components different from the ones suggested by the pilot laboratory and that were also suggested for the CIPM key comparison, like leakage, volume stability, air density, air bubbles, impurities, etc.

6.2. Major source of uncertainty

According to the uncertainty analysis provided by each participant it's possible to verify the major source of uncertainty.

As can be seen in table 4 the most important contributions are evaluated using a type-B evaluation, i.e. an estimation based on earlier experience or special judgements and not on a statistic material. The most common factor is the uncertainty in the water density or temperature, both important in transferring mass into volume. For some laboratories also the balance itself was a dominating source of uncertainty.

Table 4. Major source of uncertainty.

NMI	Major source of uncertainty
SP	Volume stability
JV	Water density
NMi VSL	Repeatability
SMU	Ambient temperature
MKEH	Impurity
PTB	Water density
SZMDM	Artefact temperature
UME	Temperature gradient within the TS
INRIM	Water density
EIM	Difference between balance reading and the filled TS
METAS	Repeatability
BEV	Water density
CMI	Balance
IPQ	Balance

7. COMPARISON WITH CIPM KCRV

The transfer standard 710-04Fyv that circulated within the European laboratories was one of three 20 L pipettes that were calibrated earlier by eight laboratories from three regional metrology organizations SIM (America), APMP (East Asia and Australia), Euramet (Europe). Three laboratories from Europe INRIM (Italy), PTB (Germany) and SP (Sweden) re-measured the changed volume of this volume standard. The outcome of both comparisons is compared graphically in figure 4.

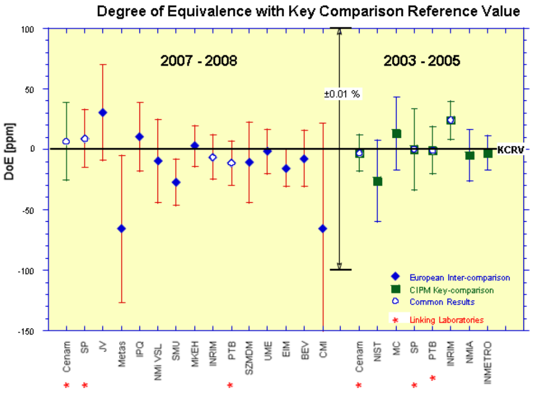

Fig. 4. Degree of equivalence with respective CIPM- KCRV.

The degree of equivalence *Di* with respect to respective reference volume as well as its uncertainty *U*(*Di*) is here expressed in relative units (parts per million). For the earlier comparison (right part) the average from three volume determinations is used for both *Di* and *U*(*Di*).

8. CONCLUSIONS

The TS had a very stable volume during the whole comparison. This was verified by two results from the pivot laboratory SP and also by CENAM, the pilot laboratory of the CIPM comparison (table 2). The results presented by the European NMIs are all consistent and overlap with the KCRV. Most results also overlap with those of the other laboratories $d_{i,j} < U(d_{i,j})$.

The volume stability of the transfer standard before and after changing its volume really admits a comparison of the two calibration lots. With the exception of two results having a larger DoE and also a larger uncertainty the outcome is very similar. The three marked laboratories make a good linkage and this is well supported by the results of the pilot.

An important outcome of this inter-comparison is that it proves the claimed capability of the calibration service in all laboratories. Actually the estimated uncertainties for this calibration and the DoE are far better than the claims. The reason for this is the exceptionally polished inner surface area that allowed an almost complete draining of the standard, giving both good repeatability and reproducibility.

For most laboratories the uncertainty budgets are similar in size, although some of them presented different components. The majority of laboratories pointed at the water density as the dominant source either directly or implicitly via the temperature measurement.

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