Instituto Português da Qualidade

SP

EURAMET Project 1008

EURAMET Regional Key Comparison

EURAMET.M.FF-K4b - Volume Inter-comparison at 20 L

EURAMET
European Association of National Metrology Institutes

Final Report

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1. Introduction

In the sequence of CIPM Key comparisons concerning volume calibrations an interregional inter-comparison CCM.FF-K4 was performed between December 2003 and March 2005 at a volume standard of 20 L and 100 mL. The corresponding regional part of this comparison within Europe was performed in 2006 for a 100 mL Gay-Lussac Pycnometer - EUROMET.M.FF-K4 (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 EURAMET.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 pivot laboratory having taken part in the interregional exercise. Fourteen countries decided to participate in this comparison. 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 European comparison measurements started in May 2007 and ended in June 2008 with a calibration at SP/Sweden. Before and after that CENAM was involved in two measurements. All four results stated a good stability of the standard.

Each participant had 3 weeks to receive the TS, make the measurements and send the TS to the next participant according to the following schedule:

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

NMI	Country	Contact	Arrival Date
CENAM	Mexico	Roberto Arias	May 2007
SP	Sweden	Peter Lau	21 May 2007
Justervesenet (JV)	Norway	Gunn Svendsen	5 July 2007
METAS	Switzerland	Hugo Bissig	6 August 2007
IPQ	Portugal	Elsa Batista	21 August 2007
NMi VSL	Netherlands	Erik Smits	3 September 2007
SMU	Slovakia	Miroslava Benkova	25 September 2007
MKEH	Hungary	Csaba Czibulka	17 October 2007
INRIM	Italy	Giorgio Cignolo	15 November 2007
PTB	Germany	Joerg Riedel	04 January 2008
SZMDM	Serbia	Branislav Tanasic	04 February 2008
UME	Turkey	Umit Akcadag	27 February 2008
EIM	Greece	Zoe Metaxiotou	28 March 2008
BEV	Austria	Wilhelm Kolaczia	14 April 2008
CMI	Czech Republic	Tomas Valenta	30 April 2008
SP	Sweden	Peter Lau	3 June 2008

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.

Each participant reported its measurement results before the end of the comparison according to a spreadsheet worked out by CENAM and supplied by the European pilot laboratory, IPQ for the European 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.

Figure 1 – 20 L pipette nº 710-04FyV

The 20 L pipette (see Fig. 1), which is made of stainless steel, has been designed to:

a) Minimize the contribution of the meniscus reading to the volume uncertainty,

b) Provide a leak-free metal to metal seal between the two parts of the container,

c) Minimize the risk of volume changes, and

d) Keep the air/liquid interface as small as possible.

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

The temperature of the water inside the TS was measured using a hand held digital thermometer coupled to fixed installed 4-wire Pt-100 temperature sensor.

A torque wrench was supplied with the transfer package to provide repeatable and reproducible torque values while assembling the transfer standard. The wrench has been set to 16 N·m for assembling purposes.

3. Conditions selected

The participating laboratories determined the volume of water that the Transfer Standard (TS) of 20 L is able to deliver after a 60 second period of dripping-off at a reference temperature of 20 °C by weighing a sampling vessel.

For the transformation from mass to volume of water the tables or formulas for the density of water [1-6] assume that the water is chemically pure; therefore, each participating laboratory ensured suitable source of water in order to make use of any of the formulas or tables.

Measurements were done after an appropriate acclimatization time (at least one-day after receipt). In particular, before the first measurement of the 20 L TS is done, it has to remain for a period of at least 12 hours in its "*filled condition*" in order to reach the necessary thermal equilibrium state and to let the water to fill out all potential cavities between the flanges.

Each participant performed 10 measurements and the results were given for a temperature of 20 ºC.

4. The experimental procedure

4.1. Experimental method

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. A summary is found in table 2.

Table 2 – Experimental method

NMI	Weighing method	Type of water	Density Formula
CENAM	Double substitution	Filtered and de-ionized	Tanaka
SP	Double substitution	De-ionised and de-aerated	Spieweck
JV	Single substitution	Purification by ion exchange and de-aerated	OIML-R49
METAS	Single substitution	Demineralised	Tanaka
IPQ	Single substitution	Distilled water	Tanaka
NMi VSL	Double substitution	Demineralised	Spieweck
SMU	Direct reading	Distilled water	Spieweck
MKEH	Substitution method	De-ionizated Water	Spieweck
INRIM	Simple substitution	De-ionised and Bi-distilled	Tanaka
PTB	Substitution method with beam scale	Distilled water	Spieweck
SZMDM	Direct reading	Distilled water	Tanaka
UME	Direct reading	Single distillation	Kell
EIM	Double substitution	De-ionization	Tanaka
BEV	Substitution method	Distilled water	Spieweck
CMI	Direct reading	Internal Procedure	Tanaka

4.2. Equipment

Each laboratory described the equipment used in the calibration and the respective traceability following a prepared form. The majority of the countries used equipment with the following characteristics:

Table 3 – Equipment characteristics

Equipment	Type	Resolution
Balance	Comparator Beam scale	(0,01 – 1) g
Weights	F1, F2, E2	-
Water thermometer in sampling vessel	Digital	(0,001 – 0,1) ºC
Air thermometer	Digital	(0,01 – 0,1) ºC
Barometer	Digital	(0,001 – 0,01) hPa
Hydrometer	Digital	(0,01 – 1) %

The last three instruments were used to calculate the air buoyancy effect. The details of the equipment used by each NMI are described in Annex 1.

4.3. Experimental conditions

The ambient conditions were described by all participants. The values given in table 4 refer to mean values.

Table 4 - Ambient conditions

NMI	Air Temperature (ºC)	Pressure (hPa)	Relative humidity (%)	Water Temperature (ºC)
CENAM	21,77	877,92	55,1	21,64
SP	21,12	997,23	37,28	20,424
JV	21,0	988,00	49,3	20,6
METAS	20,8	949,02	50,21	20,46
IPQ	21,5	1004,22	53,5	20,30
NMi VSL	20,9	1017,99	60,0	19,006
SMU	18,7	1000,18	72,6	20,268
MKEH	20,73	1004,28	49,28	19,90
INRIM	20,12	979,65	31,9	20,006
PTB	21,5	1001,78	32,8	21,164
SZMDM	20,61	1028,00	29,67	20,59
UME	20,8	991,56	54,1	20,395
EIM	21,8	1011,730	30,3	20,000
BEV	19,31	974,75	37,7	19,386
CMI	21,1	994,44	54	20,240

This comparison lasted 12 months and the measurements were performed at different altitudes above sea level what explains the differences in pressure, relative humidity and temperature.

5. Measurement 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 5 - Stability of the TS

NMI	Measurement	Date	Volume (ml)	Uncertainty (ml)	Δ*V* (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 6.

Table 6 – Volume measurement results

NMI	Volume (ml)	Uncertainty (ml)
SP*	20 002,44	0,49
JV	20 002,87	0,80
METAS	20 000,95	1,22
IPQ	20 002,47	0,58
NMi VSL	20 002,07	0,70
SMU	20 001,72	0,40
MKEH	20 002,32	0,36
INRIM*	20 002,14	0,39
PTB*	20 002,04	0,39
SZMDM	20 002,05	0,68
UME	20 002,23	0,39
EIM	20 001,95	0,33
BEV	20 002,11	0,48
CMI	20 000,95	1,74

* These laboratories took part in the CIPM – key comparison.

5.3. Determination of the regional comparison reference value - RCRV

To determine the reference value of this regional comparison the weighted mean (1) was selected, using the inverses of the squares of the associated standard uncertainties as the weights [7], according to the instructions given by the BIPM:

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

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

5.4. Determination of the uncertainty of the reference value

To calculate the standard deviation *u(y)* associated with the volume *y* [7] equation (2) was used:

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

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 [7].

$$\chi^2_{obs} = \frac{(x_1 - y)^2}{u^2(x_1)} + ... + \frac{(x_n - y)^2}{u^2(x_n)} \qquad (3)$$

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

The consistency check is regarded as failed if: $\Pr\{\chi^2(\nu) > \chi^2_{obs}\} < 0,05$

The calculated value for $\nu = 13$ $\chi^2(\nu) = 22,36 < \chi^2_{obs} = 18,99$ the observed value, 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:

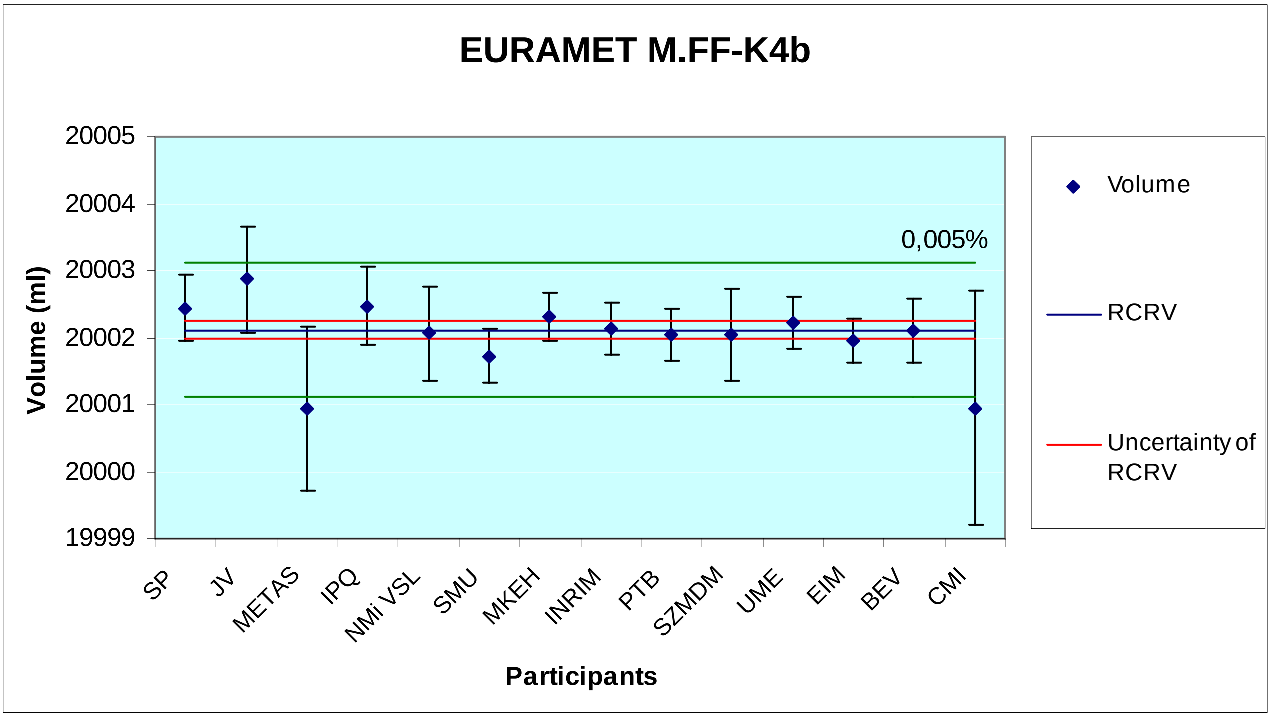

Figure 2 – Measurement results with reference value

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 (DoE) between the RCRV and the laboratories the following formula is used [7]:

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

and

$$U(d_i) = 2 \times u(d_i) \quad (5)$$

were $u(d_i)$ is given by

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

The factor 2 in equation (5) corresponds to a 95 % coverage under the assumption of normality.

The results are presented in table 7 and figure 3 in relative terms (parts per million).

The uncertainties claimed in the CMC-tables (Calibration Measurement Capability) are with one exception * taken from the BIPM homepage. They are all considerably larger than the estimated uncertainty related to this volume standard. 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.

Table 7 – Degree of equivalence with RCRV

NMI	D_i (ppm)	$U(D_i)$ (ppm)	U (CMC-claim)
SP	16	24	100
JV	38	39	60
METAS	-58	61	100
IPQ	18	28	400
NMi VSL	-2	34	100
SMU	-20	19	400
MKEH	10	17	200 *
INRIM	1	19	100
PTB	-4	18	40
SZMDM	-3	33	-
UME	6	18	200
EIM	-8	15	-
BEV	0	23	50
CMI	-58	87	100

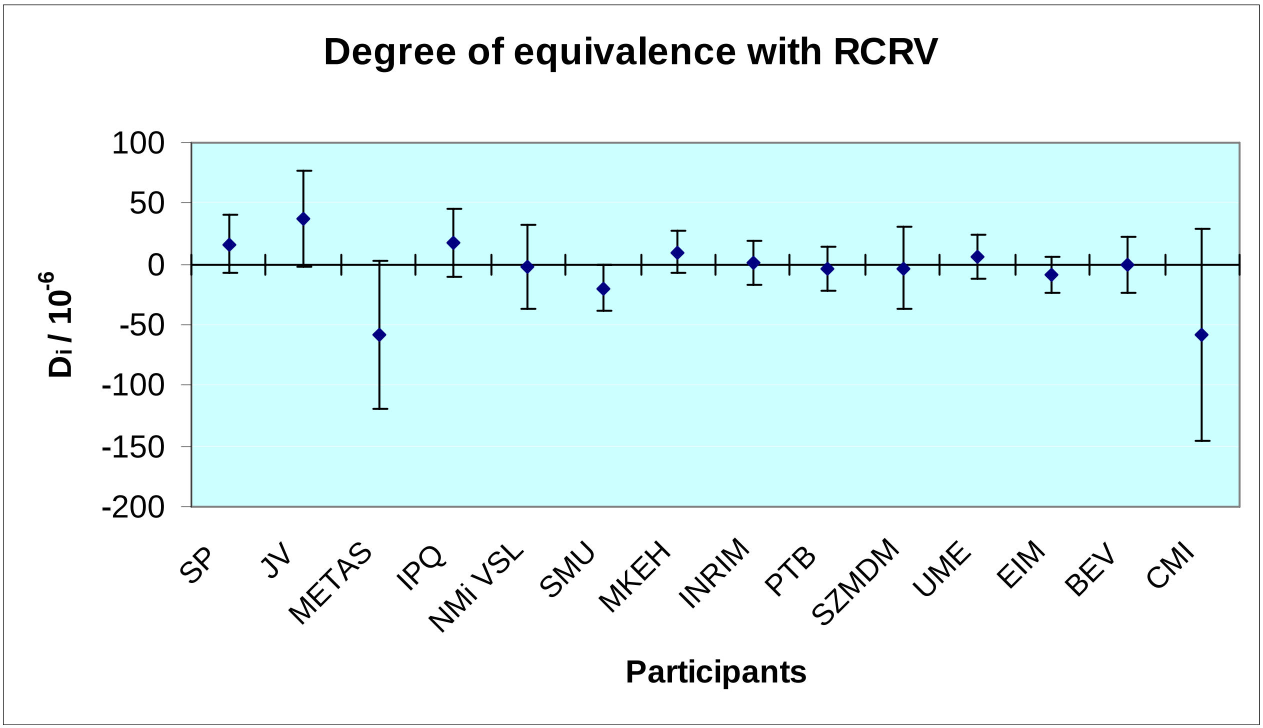

Figure 3 – Degree of equivalence with RCRV and corresponding uncertainty

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

The degree of equivalence (DoE) can also be defined between each laboratory and all other laboratories. The corresponding calculations refer to equation (7) to (9). There is a difference between equation (6) and (9). 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 (6), however, the RCRV value is not independent from each result. In contrary there is a definite correlation of the RCRV to all results, which demands for a – sign making the uncertainty in the degree of equivalence smaller than the uncertainty in each stated result.

$$d_{i,j} = x_i - x_j \tag{7}$$

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

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

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

The results of all inter-laboratory DoE are presented in the following table relating the laboratories to each other. The information in this table should be read in the following way. Compare the result of JV (maximum) in column index i = 2 with that of METAS (minimum) in row index j = 3. The number -96 indicates that METAS's volume is 96 ppm lower than JV's. The uncertainty in this difference $U(d_{ij})$ is 72 ppm. The information in cell i = 3 and j = 2 states that JV's result is 96 ppm higher. Correspondingly cell i = 1, j = 4 informs that IPQ's result is 1 ppm above SP's and the uncertainty is 38 ppm telling that both volumes are in very good agreement considering the uncertainty.

Table 8 – Inter-laboratory DoE

	SP		JV		METAS		IPQ		NMi VSL		SMU		MKEH		INRIM		PTB		SZMDM		UME		EIM		BEV		CMI	
	D_{ij}	UD_{ij}																										
	$\times 10^{-6}$																											
SP			21	46	-75	65	1	37	-19	42	-36	30	-6	29	-15	30	-20	30	-20	41	-11	30	-25	28	-17	33	-75	90
Justervesenet	-21	46			-96	72	-20	49	-40	52	-57	44	-27	43	-37	44	-41	44	-41	52	-32	44	-46	42	-38	46	-96	95
METAS	75	65	96	72			76	67	56	70	39	63	68	63	59	63	55	63	55	69	64	63	50	63	58	65	0	106
IPQ	-1	37	20	49	-76	67			-20	45	-37	34	-8	33	-17	34	-22	34	-21	44	-12	34	-26	32	-18	37	-76	91
NMi VSL	19	42	40	52	-56	70	20	45			-17	39	13	38	3	39	-1	39	-1	48	8	39	-6	38	2	41	-56	93
SMU	36	30	57	44	-39	63	37	34	17	39			30	25	21	26	16	26	16	38	25	26	11	24	19	30	-39	89
MKEH	6	29	27	43	-68	63	8	33	-13	38	-30	25			-9	25	-14	25	-14	37	-5	25	-18	23	-10	29	-68	88
INRIM	15	30	37	44	-59	63	17	34	-3	39	-21	26	9	25			-5	26	-4	38	5	26	-9	24	-1	30	-59	89
PTB	20	30	41	44	-55	63	22	34	1	39	-16	26	14	25	5	26			0	38	9	26	-5	24	3	30	-55	89
SZMDM	20	41	41	52	-55	69	21	44	1	48	-16	38	14	37	4	38	0	38			9	38	-5	37	3	41	-55	93
UME	11	30	32	44	-64	63	12	34	-8	39	-25	26	5	25	-5	26	-9	26	-9	38			-14	24	-6	30	-64	89
EIM	25	28	46	42	-50	63	26	32	6	38	-11	24	18	23	9	24	5	24	5	37	14	24			8	28	-50	88
BEV	17	33	38	46	-58	65	18	37	-2	41	-19	30	10	29	1	30	-3	30	-3	41	6	30	-8	28			-58	90
CMI	75	90	96	95	0	106	76	91	56	93	39	89	68	88	59	89	55	89	55	93	64	89	50	88	58	90		

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. The results are shown in the table 9.

The number of specified contributions in table 9 varies from 5 to 15. Generally, however, only three of them really matter. These are lighted up by colours in their importance red, yellow and pink. 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.

Table 9 – Uncertainty components

Uncertainty contributions (ml)	SP	JV	METAS	IPQ	NMi VSL	SMU	MKEH	INRIM	PTB	SZMDM	UME	EIM	BEV	CMI
Balance														
eccentricity								0,050		0,035	0,022		0,024	
resolution	0,026	0,150	0,030	0,285	0,029	0,002	0,008	0,003	0,009	0,003	0,003	0,147		0,822
linearity						0,002		0,030		0,090	0,029			
Weights (initial)											0,081			
calibration	0,0001	0,150	0,100	0,010	0,150	0,0004			0,015	0,087		0,016	0,003	
density	0,001				0,131	0,001			0,009	0,027		0,027	-0,005	
Weights (final)														
calibration		0,150	0,090			0,081	0,001	0,005				0,001		
density		0,056				0,0003	0,0001	0,007						
Water density	0,120	0,244	0,05	0,024	-0,201	0,0004	-0,032	0,120	0,151	-0,100	0,037	0,018	-0,200	0,083
Water temperature						0,000		0,012	0,014		0,055			
calibration	0,025			0,014	0,045	0,006	0,062	0,062		-0,014			0,046	0,050
Temperature gradients within the TS	0,136				0,149	0,007	0,082	0,062		-0,138	0,144	0,014	0,092	0,193
Ambient conditions														
temperature	0,015				-0,004	0,173	-0,004	0,008		-0,044	0,005		-0,020	0,009
relative humidity					-0,001	0,006	-0,095	0,004		-0,003	0,006		-0,003	0,008
pressure					0,001	0,006	0,002	0,002		0,027	0,003		0,004	0,017
Artifact														
expansion coefficient	0,025	0,040		0,013	0,040	0,00002	0,004	0,0002	0,027	-0,024	0,016	0,002	0,015	0,010
temperature	0,055	0,050				0,007	-0,014	0,095		-0,191	0,055			
Repeatability	0,021	0,110	0,590	0,050	0,050	0,040	0,023	0,065	0,054	0,035	0,046	0,057	0,070	0,179
Others	0,148	0,012		0,005	0,114		0,106		0,106	0,164		0,009	0,020	
Combined Uncertainty (ml)	0,25	0,38	0,61	0,29	0,35	0,20	0,18	0,20	0,20	0,34	0,20	0,16	0,24	0,87
Expanded uncertainty (ml)	0,49	0,80	1,22	0,58	0,70	0,40	0,36	0,39	0,39	0,68	0,39	0,32	0,48	1,74

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:

Table 10 –Major source of uncertainty

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

As can be seen from this table the most important contributions are evaluated using a type-B evaluation, i.e. an estimation based on earlier experience or special judgements and not 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.

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) in the CIPM Key comparison – CCM-FF.K4. Three laboratories from Europe INRIM (Italy), PTB (Germany) and SP (Sweden) re-measured the changed volume of this volume standard, but so did also the pilot Cenam (Mexico). The outcome of both comparisons is presented graphically in figure 4.

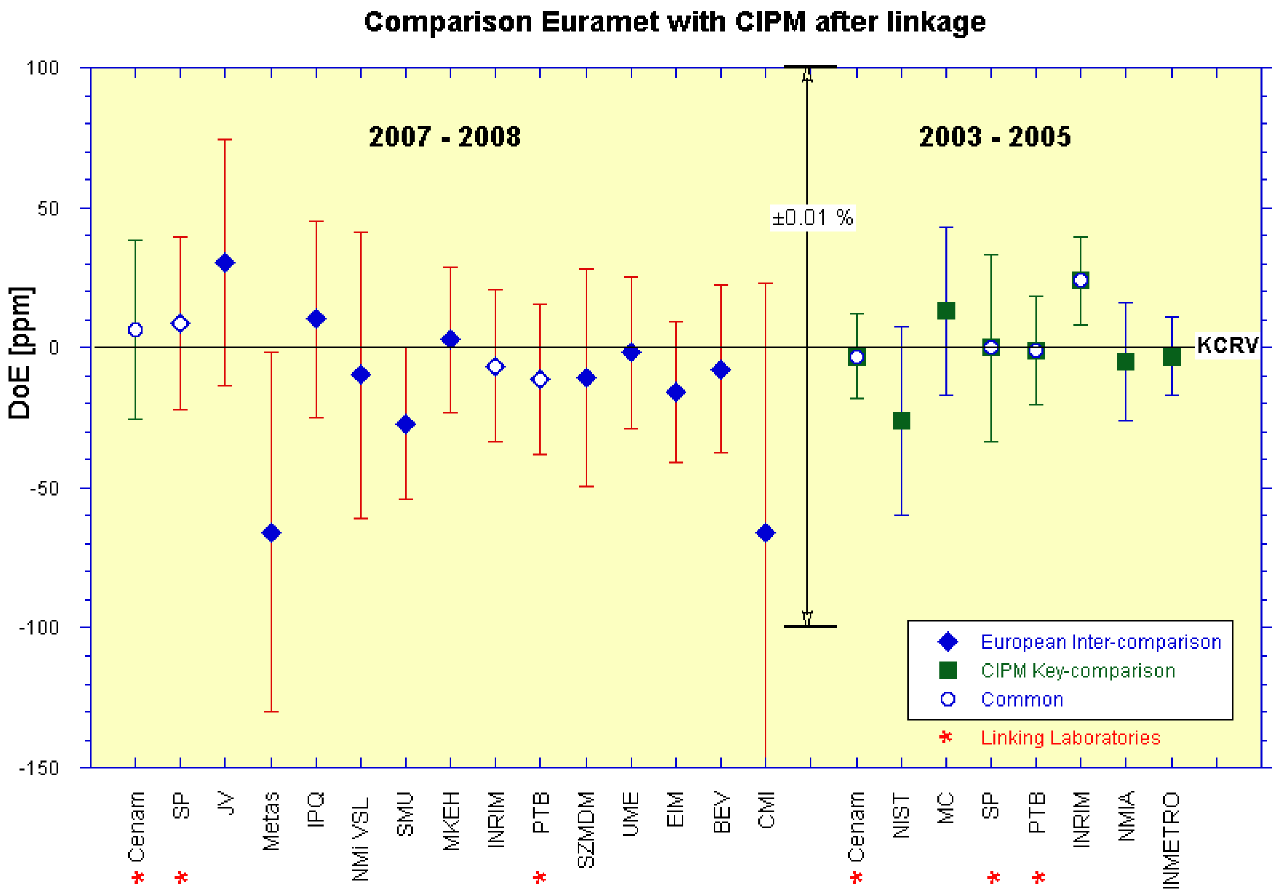

Figure 4 – Degree of equivalence with respect to the KCRV and it's uncertainty in parts per million.

The degree of equivalence D_i referring to the key comparison reference value, but based on the calibration of different volume standards, and also the uncertainty $U(D_i)$ including the linkage is here expressed in relative units (parts per million). For the earlier comparison (right part establishing the KRCV) the average from the calibration of three volume standards is used for both D_i and $U(D_i)$. It is also possible to relate each laboratory's result to every other laboratory result as explained in 5.6. A table for all these degrees of equivalence is contained in Annex 2.

The basic idea was to use the three European laboratories (SP, PTB, INRIM) for linking all European results to the Key Comparison Reference Value. However, there are metrological arguments for a different choice. For the actual TS used in the European round robin SP had a clear outlier in the key-comparison. The linking can not be based on the contained volume of the TS as it was deliberately changed by the pilot for the regional comparison. Thus linking has to be arranged in relative terms via the degree of equivalence. The best representative for the key comparison is the average degree of equivalence for three TS's. Cenam is a fourth laboratory having taken part in both exercises. As figure 5 shows the three average results of Cenam ,SP and PTB are metrologically identical and very close to the KCRV, whereas two of INRIM's three results were not consistent with the rest.

Therefore the linking procedure is made up in the following way. For both comparisons a degree of equivalence for linking is constructed as the weighted mean (equation (1)) of the laboratories that stand the consistency test (Cenam, SP and PTB). This is shown in figure 5 as DoE(link)KCRV on the left side and as DoE(link)RCRV on the right side together with the calculated uncertainties (equation (2)). Linking now means the two base lines graphically adjust the results of the two comparisons to each other.

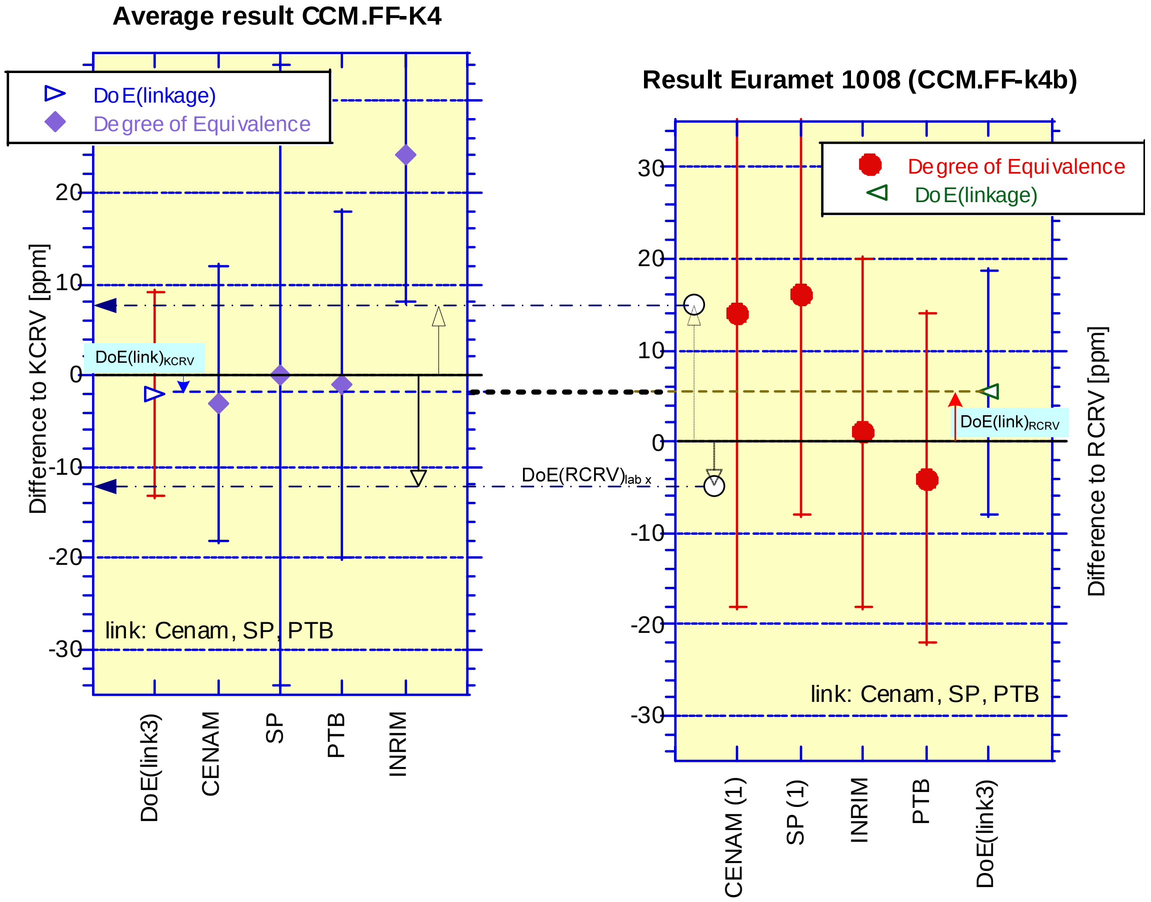

Figure 5 - Linking procedure to the KCRV using a base line built on three laboratory results

With the equality of $DoE(link)_{KCRV}$ and $DoE(link)_{RCRV}$ any regional result can be related to the key comparison and the KCRV by a simple transformation.

Let $DoE(RCRV)_{labx}$ be the result for any laboratory x in the European inter-comparison.
Let $DoE(KCRV)_{labx}$ be the interesting degree of equivalence for this laboratory with respect to the key comparison. Equation (10) forms the transformation between the two.

$$DoE(KCRV)_{lab\,x} = DoE(RCRV)_{lab\,x} - DoE(link)_{RCRV} + DoE(link)_{KCRV} \quad (10)$$

or simpler

$$DoE(KCRV)_{lab\,x} = DoE(RCRV)_{lab\,x} + DoE(link)$$

with

$$DoE(link) = -DoE(link)_{RCRV} + DoE(link)_{KCRV} \quad (11)$$

as the displacement from the regional to the key comparison reference value.

The linkage of course introduces additional uncertainties, which are related to the uncertainties in the two base lines $DoE(link)_{KCRV}$ and $DoE(link)_{RCRV}$ and which must be observed when expressing the degree of equivalence to the key comparison reference value. These two are calculated according to equation (6). An uncertainty for the linking must however also embrace alternative choices of linking laboratories. This aspect is respected by looking at the range of possible values for DoE(link) with different laboratory constellations and considering these as rectangular distributed. Assuming no correlation the combined standard uncertainty related to the adjustment between the two comparisons then is 9,9 ppm, which has to be combined with the uncertainties found in the DoE for the regional comparison.

Table 11 –Data for linking and two example results

	Value [ppm]	Standard uncertainty [ppm]
DoE(link)$_{RCRV}$	5,38	6,61
DoE(link)$_{KCRV}$	-1,99	5,56
Choice of linking laboratory	-	4,86
DoE(link)	-7,37	9,91

Example:

DoE(RCRV)$_{labx}$	-5	18
DoE(KCRV)$_{labx}$	-12,37	21
DoE(RCRV)$_{laby}$	15	25
DoE(KCRV)$_{laby}$	7,63	27

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 5).

The results presented by the European NMIs are all consistent and overlap with the RCRV. Most results also overlap with those of the other laboratories $d_{i,j} < U(d_{i,j})$.

The excellent repeatability and good volume stability of the transfer standard before and after changing its volume really admits a comparison of the two calibration lots and thus a linking to a key comparison reference value. With the exception of two results having a larger DoE and also a larger uncertainty the outcome from both round robins is very similar. It is important to notice that the generally larger uncertainties in the European results include an additional linking uncertainty to the KCRV of 20 ppm at a 95 % coverage level.

The stability of the TS is of course essential, but equally important is that the laboratories on which the linking relies did not change anything in their procedures or equipment between the two exercises. In this project actually four laboratories were available for linking. As mentioned earlier the natural choice had been to use the three European participants common in both comparisons. But the relation between their results did shift noticeably (figure 5). The relation between Cenam and SP on the other hand had been remarkably stable, which is impressive when referring to table 5. This argument together with the closeness in three separate calibrations between Cenam, PTB and SP during the key comparison and Inrim being noticeably shifted suggest that the three laboratories marked with a star in figure 4 make the most reliable linkage between the regional- and the key-comparison.

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 very good repeatability and reproducibility.

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

9. References

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Annex 1 - Equipment

Balance

NMI	Manufacturer	Type	Upper range Value (kg)	Resolution (g)	Standard uncertainty (g)	Calibration date	Traceability
SP	Mettler	KA30-31	30	0,005	0,02	21-12-2007	SP - MTmF718454-08
JV	Mettler	ID5	600	0,1	---	---	---
METAS	Mettler-Toledo	KA50	---	0,005	0,0007	---	This balance is not calibrated as it is use calibrated weights. We determine the weight of the sample by means of comparison to the calibrated weights
IPQ	Mettler	KCC100-2	150	0,05	0,6	15-01-2007	IPQ
NMi VSL	Mettler-Toledo	KCC100-2	150	0,05	---	---	NMi VSL
SMU	Mettler-Toledo	XP64001L	64,1	0,1	3,5	15-11-2006	Mass standarts SMU, P5, P6, P7, 002 (10kg - 1kg) Certificate No: 12/220/12/06
MKEH	Mettler-Toledo	XP 64002L	64,1	0,01	0,015 - 0,025	2007	MKEH
INRIM	Mettler	PK60 Spezial	60	0,01	Depends on weighing method	06-02-2006	INRIM
PTB	Sartorius	beam scale	50	0,005	0,018	Jan-07	PTB
SZMDM	Sartorius	CC50000	60	0,01	0,097	Fev-08	SZMDM
UME	Sartorius AG	CC 30002	41	0,005	0,075	28-02-2008	UME
EIM	Mettler-Toledo	KA30-3	32	0,005	0,058	09-04-2008	EIM
BEV	Precisa	30000D SCS	30	0,01	0,02	13-09-2004	BEV
CMI	Mettler-Toledo	ID5 MultiRange/ KCC150	150	1	0,82	21-01-2008	CMI

Weights

NMI	Manufacturer	Type	Upper range Value (kg)	Resolution (g)	Standard uncertainty (g)	Calibration date	Traceability
CEM	Masstech	F1	5	---	0,004	05-09-2005	CENAM
CEM	Insco	F1	20	---	0,016	28-02-2007	CENAM
SP	Z-set	20 kg	N. A.	not appl.	0,05	27-09-2007	SP - MTmF718454-01
SP	Z-set	5 kg	N. A.	not appl.	0,013	27-09-2007	SP - MTmF718454-01
SP	V-set	1 kg	N. A.	not appl.	0,0025	28-09-2007	SP - MTmF718454-02
SP	V-set	500 g	N. A.	not appl.	0,0013	28-09-2007	SP - MTmF718454-02
SP	V-set	200 g	N. A.	not appl.	0,0005	28-09-2007	SP - MTmF718454-02
SP	V-set	100 g	N. A.	not appl.	0,00025	28-09-2007	SP - MTmF718454-02
JV	Unknown	F1	N. A.	20000	0,01	15-05-2007	JV (National Standard Mass)
METAS	402	0,05 kg	---	---	0	03-03-2003	---
METAS	402	0,1 kg	---	---	0,00002	03-03-2003	---
METAS	401º	0,5 kg	---	---	0,00008	21-01-2003	---
METAS	401º	2 kg	---	---	0,001	21-01-2003	---
METAS	401º	10 kg	---	---	0,0025	21-01-2003	---
METAS	400	10 kg	---	---	0,003	03-08-2003	---
IPQ	Sartorious	F1	N. A.	---	0,02	07-06-2005	PTB
NMi VSL	---	OIML class F2	---	---	See F2	06-03-2007	NMi VSL
SMU	MTT	1, 2, 2, 5, 10 kg	N. A.	---	0,00075 - 0,0075	01-02-2006	Mass standard SMU, P7 (10 kg - 1 kg), Certificate Nº: e4/220/12/06
MKEH	Kern	E2	0,001 - 0,5	---	1,5E-6 - 2,5E-5	2003	MKEH
MKEH	Häfner	E2	20	---	0,5 mg	2006	MKEH
INRIM	Häfner	10 kg OIML F1	N. A.	not appl.	0,0005 (10kg)	13-10-2004	INRIM
PTB	Kern	F1	N. A.	---	---	Mai-92	PTB
SZMDM	Sartorius	---	N. A.	E2	---	Fev-08	PTB
UME	Hafner	E2 Class	N. A.	---	0,001	09-01-2004	UME
EIM	Häfner	F1	N. A.	---	---	18-12-2007	BIPM
BEV	Kern	F1	N. A.	5000	0,002	03-04-2008	BEV

Temperature

NMI	Manufacturer	Type	Upper range Value	Resolution	Standard uncertainty	Calibration date	Traceability
SP	Testo	Testo 610	N. A.	0,1 ºC	0,08 ºC	11-12-2006	SP - ETksF625528-3
JV	Vaisala	PTU200	N. A.	0,1 ºC	0,1 ºC	25-06-2007	JV (Fixpoints)
METAS	Rotronic, Bassersdorf (CH)	Thermo-Hygrometer; Hygroskop DV2	---	0,1 ºC	0,2 ºC	08-11-2005	151-03684
IPQ	Hygroclip	Electronic	N. A.	0,1 ºC	0,5 ºC	21-02-2006	IPQ
NMi VSL	Novasina	HygroDat 100	30 ºC	0,1 ºC	0,05 ºC	01-02-2007	NMi VSL
SMU	Thermometer Precisa	ad 3000 th	N. A.	0,001 ºC	0,006 ºC	25-01-2007	National standart SMU No.020/A, Certificate No: 021/270/32/07
MKEH	Ahlborn	Almemo 2290-2	---	0,01 ºC	0,01 ºC	2007	MKEH
INRIM	Corradi	RP2000DS	N. A.	10 mK	20 mK	30-10-2007	INRIM
PTB	Testo	600	N. A.	0,1 ºC	0,5 ºC	Mai-05	PTB
SZMDM	Cole-Parmer, USA	03313-65	N. A.	0,01 ºC	0,03 ºC	19-04-2005	NIST
UME	Vaisala	HMI 36	N. A.	0,1 ºC	0,3 ºC	07-01-2008	UME
EIM	Rotronic A.G	BT-RS1	N. A.	100 mK	70 mK	09-04-2008	EIM
BEV	Isotech Pt25	909	N. A.	0,1 mK	1 mK	12-02-2008	BEV
CMI	COMET Systém	THPZ	N. A.	0,1 ºC	0,12 ºC	01-11-2007	CMI

Air pressure

NMI	Manufacturer	Type	Upper range Value (Pa)	Resolution (Pa)	Standard uncertainty (Pa)	Calibration date	Traceability
SP	Paulin	Linod	N. A.	20	16	21-12-2006	0630 957
JV	Vaisala	PTU200	N. A.	10	19	17-01-2006	LNE (France)
METAS	Thommen AG, Waldenburg	Barometer Type 2A4.811.0 2, S/N 235544	---	20	100	25-11-2007	Internal protocol
IPQ	Druck	DPI142	N. A.	1	---	---	---
NMi VSL	Druck	DPI 142	106000	1	4	31-01-2007	NMi VSL
SMU	ILLMENAU	B2	N. A.	10	33	22-06-2007	Pressure Standart SMU No. 020/A, Certificate No: 142/220/17/0 7
MKEH	Wallace & Tiernan	Diptron 3+	---	10	10	2007	MKEH
INRIM	Ruska	PPG6220	N. A.	0,1	1,5	25-05-2006	INRIM
PTB	Setra	370	N. A.	1	2	Set-04	PTB
SZMDM	VEB FEINGERATEBA U, Germany	104	N. A.	100	129	Jan-08	SZMDM
UME	Setra	370	N. A.	1	2	10-12-2007	UME
EIM	Lufft	Barometer	N. A.	5	35	---	PTB
BEV	Vaisala	Z 191 0003	N. A.	1	20	22-07-2004	BEV
CMI	COMET Systém	THPZ	N. A.	10	79	01-11-2007	CMI

Humidity

NMI	Manufacturer	Type	Upper range Value	Resolution (%)	Standard uncertainty (%)	Calibration date	Traceability
SP	Testo	Testo 610	N. A.	0,1	0,4	11-12-2006	SP - ETksF625528-3
JV	Vaisala	PTU200	N. A.	0,1	0,9	25-06-2007	NPL (UK)
METAS	Rotronic, Bassersdorf (CH)	Thermo-Hygrometer; Hygroskop DV2	---	0,1	1	08-11-2005	151-03684
IPQ	Hygroclip	Electronic	N. A.	0,1	1	21-02-2006	IPQ
NMi VSL	Novasina	HygroDat 100	70%	0,1	0,3	01-02-2007	NMi VSL
SMU	Ahlborn	RH Sound H029245G	N. A.	0,1	1,75	24-01-2007	Reference standart SMU, Certificate No: 50/260/34/07
MKEH	Ahlborn	Almemo 2290-2	---	0,01	0,6	2007	MKEH
INRIM	Vaisala	HMP 233	N. A.	0,1	0,17	24-04-2007	INRIM
PTB	Testo	600	N. A.	0,1	0,5	Mai-05	PTB
SZMDM	Cole-Parmer, USA	03313-65	N. A.	0,01	0,44	19-04-2005	NIST
UME	Vaisala	HMI 36	N. A.	0,1	1,3	07-01-2008	UME
EIM	Rotronic A.G.	BT-RS1	N. A.	0,1	0,35	09-04-2008	EIM
BEV	Vaisala	HMP231	N. A.	0,1	0,4	14-09-2004	BEV
CMI	COMET Systém	THPZ	N. A.	1	4,2	02-11-2007	CMI

Annex 2 – Degree of Equivalence

Lab j ⟹

Lab i ↓

Lab i			SP		JV		Metas		IPQ		NMiVSL		SMU		MKEH		INRIM		PTB		SZMDM		UME	
	D_i	$U(D_i)$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$
	$*10^{-6}$		$*10^{-6}$																					
SP	9	31			21	46	-75	65	1	37	-19	42	-36	30	-6	29	-15	30	-20	30	-20	41	-11	30
JV	30	44	-21	46			-96	72	-20	49	-40	52	-57	44	-27	43	-37	44	-41	44	-41	52	-32	44
Metas	-66	64	75	65	96	72			76	67	56	70	39	63	68	63	59	63	55	63	55	69	64	63
IPQ	10	35	-1	37	20	49	-76	67			-20	45	-37	34	-8	33	-17	34	-22	34	-21	44	-12	34
NMi VSL	-10	40	19	42	40	52	-56	70	20	45			-17	39	13	38	3	39	-1	39	-1	48	8	39
SMU	-27	27	36	30	57	44	-39	63	37	34	17	39			30	25	21	26	16	26	16	38	25	26
MKEH	3	26	6	29	27	43	-68	63	8	33	-13	38	-30	25			-9	25	-14	25	-14	37	-5	25
INRIM	-7	27	15	30	37	44	-59	63	17	34	-3	39	-21	26	9	25			-5	26	-4	38	5	26
PTB	-11	27	20	30	41	44	-55	63	22	34	1	39	-16	26	14	25	5	26			0	38	9	26
SZMDM	-11	39	20	41	41	52	-55	69	21	44	1	48	-16	38	14	37	4	38	0	38			9	38
UME	-2	27	11	30	32	44	-64	63	12	34	-8	39	-25	26	5	25	-5	26	-9	26	-9	38		
EIM	-16	25	25	28	46	42	-50	63	26	32	6	49	-11	24	18	23	9	24	5	24	5	37	14	24
BEV	-8	30	17	33	38	46	-58	65	18	37	-2	52	-19	30	10	29	1	30	-3	30	-3	41	6	30
CMI	-66	89	75	90	96	95	0	106	76	91	56	98	39	89	68	88	59	89	55	89	55	93	64	89
Cenam	-3	15	12	34	33	47	-63	66	13	38	-7	53	-24	31	6	30	-4	31	-8	31	-8	42	1	31
NIST	-26	34	35	46	56	56	-40	72	36	48	16	61	-1	43	29	43	19	43	15	43	15	51	24	43
MC	13	30	-4	43	17	53	-79	70	-3	46	-23	59	-40	40	-10	40	-20	40	-24	40	-24	49	-15	40
SP	0	34	9	46	30	55	-66	72	10	48	-10	61	-27	43	3	42	-7	43	-11	43	-11	51	-2	43
PTB	-1	19	10	36	31	48	-65	67	11	40	-9	54	-26	33	4	32	-6	33	-10	33	-10	43	-1	33
INRIM	24	16	-15	35	6	47	-90	66	-14	38	-34	53	-51	31	-21	30	-31	31	-35	31	-35	42	-26	31
NMIA	-5	21	14	37	35	49	-61	67	15	41	-5	55	-22	35	8	34	-2	34	-6	34	-6	44	3	34
INMETRO	-3	14	12	34	33	46	-63	65	13	37	-7	52	-24	31	6	30	-4	31	-8	30	-8	41	1	30

Lab j →

Lab i ↓

Lab i			EIM		BEV		CMI		CENAM		NIST		MC		SP		PTB		INRIM		NMIA		INMETRO	
	D_i	$U(D_i)$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$
	$*10^{-6}$		$*10^{-6}$																					
SP	9	31	-25	28	-17	33	-75	90	-12	34	-35	46	4	43	-9	46	-10	36	15	35	-14	37	-12	34
JV	30	44	-46	42	-38	46	-96	95	-33	47	-56	56	-17	53	-30	55	-31	48	-6	47	-35	49	-33	46
Metas	-66	64	50	63	58	65	0	106	63	66	40	72	79	70	66	72	65	67	90	66	61	67	63	65
IPQ	10	35	-26	32	-18	37	-76	91	-13	38	-36	48	3	46	-10	48	-11	40	14	38	-15	41	-13	37
NMi VSL	-10	51	-6	49	2	52	-56	98	7	53	-16	61	23	59	10	61	9	54	34	53	5	55	7	52
SMU	-27	27	11	24	19	30	-39	89	24	31	1	43	40	40	27	43	26	33	51	31	22	35	24	31
MKEH	3	26	-18	23	-10	29	-68	88	-6	30	-29	43	10	40	-3	42	-4	32	21	30	-8	34	-6	30
INRIM	-7	27	-9	24	-1	30	-59	89	4	31	-19	43	20	40	7	43	6	33	31	31	2	34	4	31
PTB	-11	27	-5	24	3	30	-55	89	8	31	-15	43	24	40	11	43	10	33	35	31	6	34	8	30
SZMDM	-11	39	-5	37	3	41	-55	93	8	42	-15	51	24	49	11	51	10	43	35	42	6	44	8	41
UME	-2	27	-14	24	-6	30	-64	89	-1	31	-24	43	15	40	2	43	1	33	26	31	-3	34	-1	30
EIM	-16	25			8	28	-50	88	13	29	-10	42	29	39	16	42	15	32	40	29	11	33	13	29
BEV	-8	30	-8	28			-58	90	5	34	-18	45	21	43	8	45	7	36	32	34	3	37	5	34
CMI	-66	89	50	88	58	90			-23	90	40	95	79	94	66	95	65	91	90	90	61	92	63	90
Cenam	-3	15	-13	29	-5	34	23	90			-23	37	16	33	3	37	2	25	27	22	-2	26	0	21
NIST	-26	34	10	42	18	45	-40	95	23	37			39	45	26	48	25	39	50	37	21	40	23	36
MC	13	30	-29	39	-21	43	-79	94	-16	33	-39	45			-13	45	-14	35	11	34	-18	37	-16	33
SP	0	34	-16	42	-8	45	-66	95	-3	37	-26	48	13	45			-1	39	24	37	-5	40	-3	36
PTB	-1	19	-15	32	-7	36	-65	91	-2	25	-25	39	14	35	1	39			25	25	-4	29	-2	24
INRIM	24	16	-40	29	-32	34	-90	90	-27	22	-50	37	-11	34	-24	37	-25	25			-29	26	-27	21
NMIA	-5	21	-11	33	-3	37	-61	92	2	26	-21	40	18	37	5	40	4	29	29	26			2	25
INMETRO	-3	14	-13	29	-5	34	-63	90	0	21	-23	36	16	33	3	36	2	24	27	21	-2	25		