Final Report
on

Regional Key Comparison for Volume of liquids at 20 L and 100 mL

Conducted January 2007 to December 2008

SIM.M.FF-K4

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CONTENT

1. INTRODUCTION

At its meeting in October 2006 in Querétaro, México, the Interamerican Metrology System (SIM) Technical Committee for Fluid Flow (TCFF) approved a Regional Key Comparison for Volume of Liquids at 20 L and 100 mL, to be piloted by the National Metrology Institute of Mexico (CENAM). The objective of this comparison is to demonstrate the degree of equivalence of the volume measurement standards held at National Measurement Institutes (NMIs) and to provide supporting evidence for the calibration and measurement capabilities (CMCs) claimed by the participating laboratories in the Americas.

The volume comparison is identified as SIM.M.FF-K4 and performed with the intention to compare the performance of volume of liquid measurements, using a 20 L test measure and two 100 mL test measures, and to link the comparison results to the corresponding CIPM key comparison, CCM.FF-K4.

During the comparison, one of the pycnometers (serial 03.04.15) suffered an irreversible damage; this occurred after INDECOPI tests. Therefore, pycnometer 03.01.15 was tested by CENAM, JSB, LACOMET, CENAMEP and INDECOPI; this transfer standard was replaced by pycnometer 03.01.17, which was measured by CENAM, IBMETRO, LATU, INTI and INMETRO. Pycnometer 03.04.04 was measured by all participants.

RCRV and Degrees of Equivalence $\boldsymbol{d_i}$, for volume at 100 mL were calculated using the results for Pycnometer 03.04.04.

2. CONDITIONS SELECTED

The participating laboratories determined the volume of water that the 20 L Transfer Standard (TS) is able to **deliver** after a 60 second period of dripping-off at a reference temperature of 20 °C; as well as to determine the volume of water that each of the two Transfer standards of 100 mL - glass pycnometers of the Gay-Lussac type – is able to **contain,** at a reference temperature of 20 °C.

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 performed after an appropriate acclimatization time (at least one-day after receipt). In particular, before the first measurement on the 20 L TS was done, it had 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.

Transfer package for 100 mL did not include temperature measurement system. It was up to the participating laboratories to measure water temperature according to their own facilities and procedures.

The pilot laboratory collected and analyzed the results according to MRA procedures. Draft B is intended to be a publication for the CIPM Key Comparison Data Base.

3. PARTICIPANTS AND SCHEDULE

Each laboratory was responsible for receiving the Transfer Packages, testing and sending them to the next participant according to the schedule.

Table 1 List of the participating NMI, along with technical contacts.

#	NMI		Date month/day, year	Contact	Remarks
1	CENAM	Mexico	January 2007	Roberto Arias rarias@cenam.mx	Pilot, CCM.FF-K4 link
2	NIST	USA	March 2007	John D. Wright john.wright@nist.gov	SIM participant, CCM.FF-K4 link
3	BSJ	Jamaica	April 2007	Tanisha Wallace TWallace@bsj.org.jm	SIM participant
4	LACOMET	Costa Rica	June 2007	Sandra Rodríguez/Humberto Murillo srodriguez@lacomet.go.cr hmora@lacomet.go.cr	SIM participant
5	CENAMEP	Panama	August 2007	Orlando Pinzón opinzon@cenamep.org.pa	SIM participant
7	INDECOPI	Peru	October 2007	Abed Morales amorales@indecopi.gob.pe	SIM participant
8	IBMETRO	Bolivia	February 2008	María Vega mvega@ibmetro.gob.bo	SIM participant
9	LATU	Uruguay	April 2008	Claudia Santo csanto@latu.org.uy	SIM Participant
9	INTI	Argentina	August 2008	Fernando Kornblit ferk@inti.gov.ar	SIM Participant
10	INMETRO	Brazil	October 2008	Dalni Malta dsfilho@inmetro.gov.br	SIM participant, CCM.FF-K4 link
	CENAM	Mexico	December 2008	Roberto Arias	

4. THE TRANSFER PACKAGES

4.1 Transfer Package for 20 L

The TS consisted of: a) the 20 L pipette, b) a hand held digital thermometer, c) fittings for assembling and disassembling. Appendix A lists details for the components of the transfer package.

The 20 L pipette (**see Fig. 1**), which is made of stainless steel, was 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 features were intended to produce repeatable and reproducible volume measurement values on the order of 0,005 %, or better.

Temperature of the water inside the TS was measured by a hand held digital thermometer coupled with 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 was set to 33.9 N·m for assembling purposes.

4.2 Transfer Package for 100 mL

The Transfer Standards for volume at 100 mL are commercially available glass pycnometers (Gay Lussac Type, **see Fig. 2**). Made out of boro-silicate glass, they were manufactured according to ISO 3507.

A set of two pycnometers of 100 mL were calibrated and results given for a reference temperature of 20 °C. Each participating laboratory measured water temperature using its own instruments and procedures.

The linear coefficient of expansion for the boro-silicate glass was provided by the manufacturer as $3.3 \cdot 10^{-6}$ °C^{-1}; this value is transformed to a cubic expansion coefficient of $(9.9 \pm 1) \cdot 10^{-06}$ °C^{-1}.

5. MEASUREMENT PROGRAM

Each participating laboratory tested each transfer standard so that 10 measurements were performed for each artifact. Table 2 shows an example of the testing program.

Table 2 Example of the data sheet from the testing program.

		Day of test					
		1	2	3	4	5	6
Measurements per day	1	Reception and inspection	Experimental set-up and Acclimatization	x_1	x_1		Packaging of the TSs for shipment to next NMI.
	2			x_2	x_2		
	3			x_3	x_3		
	4			x_4	x_4		
	5			x_5	x_5		

	$x_i = \frac{1}{10}\sum_{i=1}^{10} x_i$; x_i are results referenced to 20° C.

6. EXPERIMENTAL PROCEDURE

All of the participating NMIs did apply gravimetric techniques to determine the volume of water. Density of the water was determined by using different formulations (see table 3). In the case of the 20 L TSs, use of an auxiliary reservoir was necessary to determine the volume of water delivered by the TSs.

Table 3 Summary of the experimental procedure employed at the different NMIs

		Weighing*		**Water****	**De-aerated water?**	**Density formula**
		20 L	100 mL			
CENAM	1	DS	DR	IE + O	No	Tanaka [1]
NIST	2	DR		1D	No	Patterson [5]
BSJ	3	SS	RTR	1D	No	Tanaka [1]
LACOMET	4	DS	DS	2D	No	Tanaka [1]
CENAMEP	5	DS	DR	D+I	No	Tanaka [1]
INDECOPI	6	SS	DR	1D	No	Bettin [2]
IBMETRO	7	DS	DS	D+I	No	Tanaka [1]
LATU	8	DR	DR	2D	No	Tanaka [1]
INTI	9	DS	DS	1D	Yes	Tanaka [1]
INMETRO	10	SS/ABA	DR	2D+I	Yes	Tanaka [1]

***Weighing:** *DS*: Double substitution; *DR*: direct reading; *SS*: single substitution; *RTR*: Reference-test-reference
****water:*** IE: Ion exchange; O: Inverse osmosis; 1D: single distillation; 2D: double distillation; D+I: Distilled and Ionized

Appendix B includes the traceability and uncertainty statements for each of the key measuring instruments that were employed at each of the participating NMIs.

No mathematical expression was provided or suggested in the technical protocol to evaluate the measurand; each participant made use of its own methods to determine the volume of water from mass and density determinations.

For measurements at 100 mL some of the participants decided to adjust the meniscus of the pycnometer while being partially submerged into a thermostatic bath at the reference temperature. However, this is not practical for measurements at 20 L; in this sense, stability of the environmental conditions could impair the uncertainty values. Table 4 shows a summary of the thermal stability at the different participating laboratories.

Table 4 Summary of the thermal stability within the laboratories. ***T_d* - 20** represents the absolute difference between the temperature of the device under test (20 L TS) and the reference temperature. ***T_w* - *T_a*** represents the difference between water and ambient temperature.

Measurements at 20 L	1	2	3	4	5	6	7	8	9	10
	ºC									
$\lvert T_d - 20 \rvert$	0.53	0.28	0.61	0.53	0.73	0.49	0.12	0.80	0.05	0.01
$\lvert T_w - T_a \rvert$	0.38	2.28	0.81	1.08	0.53	0.49	0.58	0.80	0.51	0.12

7. RESULTS

7.1 Stability of the TSs

CENAM as the pilot laboratory tested all artifacts before and after the comparison. The results of the testing are given in tables 5 and 6. Initial test values correspond to the official measurements results of CENAM; only these results are taken into consideration for the calculation of the Regional Comparison Reference Value (RCRV).

Table 5 Stability of the 20 L TSs, according to the measurement results obtained at the pilot laboratory.

20 L	date	Initial		date	final		$\lvert\Delta V\rvert$
		x_i, $u(x_i)$,* [mL]			x_i, $u(x_i)$, [mL]		mL
TS 710-05	January 2007	19 995.03	0.24	December 2008	19 995.2	0.25	0.17

Table 6 Stability of the 100 mL TSs, according to the measurement results obtained at the pilot laboratory.

100 mL	date	Initial		date	Final		$\lvert\Delta V\rvert$
		x_i, $u(x_i)$, [mL]			x_i, $u(x_i)$, [mL]		mL
TS 03.04.04	January 2007	99.080 2	0.001 6	December 2008	99.081 2	0.001 7	0.001 0
TS 03.01.15	January 2007	97.953 4	0.001 6				
TS 03.01.17	January 2008	100.927 6	0.001 5	December 2008	100.929 2	0.001 7	0.001 6

* ***$u(x_i)$*** is the ***k*** = 1, approximately 67 % confidence level, or standard uncertainty, ***$U(x_i)$*** is the ***k*** = 2, approximately 95 % confidence level, or expanded uncertainty.

No substantial drift was observed either on the 20 L TS or on the 100 mL TSs; the initial and final measurements at the pilot NMI showed to be consistent with each other. Therefore, no additional contribution of uncertainty due to drift will be included when calculating ***RCRVs***.

It is to be noted that NIST did not tested the 100 mL artifacts; NIST Technical Contact explained that they are not including calibration services of glassware in their corresponding CMCs list. Therefore, 20 L TS were tested by 10 participants, whereas 100 mL TSs by 9 NMIs.

7.2 Results reported by the participants

Tables 7 and 8 show the measurement results and standard uncertainties as reported by the participants.

Table 7 Reported results for 20 L TSs (artifact 710-05)

20 L TS	**TS 710-05**	
	x_i, [mL]	$u(x_i)$, [mL]
CENAM	19 995.03	0.25
NIST	19 995.79	0.59
BSJ	19 996.62	6.40
LACOMET	19 990.39	1.46
CENAMEP	19 995.47	0.53
INDECOPI	19 994.45	0.89
IBMETRO	19 994.18	0.96
LATU	19 993.50	0.59
INTI	19 995.04	0.12
INMETRO	19 995.06	0.23

	RCRV [mL]	*U(RCRV)* [mL]
RCRV	**19 994.9**	**0.46**
Method	Median	

When calculating the ***RCRV*** by the Cox method, denoted as *w-m*, two values were found to be discrepant. LACOMET and LATU values were qualified as discrepant for TS 710-05. Attempts were made to resolve the inconsistency; however, after reviewing their calculations, no errors were found by LACOMET nor LATU. Therefore, the median was selected as method for estimating the ***RCRV***, computed by means of the Monte Carlo Method. 20 000 trials were produced for generating the corresponding ***pdf***.

Appendix C contains details of the resultant ***RCRV pdf*** for volume of liquids at 20 L, as produced by the Monte Carlo Method. The computation of degrees of equivalence $\boldsymbol{d_i}$ and its associated uncertainty $\boldsymbol{u(d_i)}$ has been computed also by Monte Carlo Method.

Table 8 Reported results for 100 mL TSs (artifacts 03.04.04, 03.01.15 and 03.01.17)

100 mL TSs	**TS 03.04.04**		**TS 03.01.15**		**TS 03.01.17**	
	x_i, [mL]	$u(x_i)$, [mL]	x_i, [mL]	$u(x_i)$, [mL]	x_i, [mL]	$u(x_i)$, [mL]
CENAM	99.080 2	0.001 6	97.953 4	0.001 6	100.927 6	0.001 5
BSJ	100.130 7	0.037	99.0639	0.020		
LACOMET	99.081 8	0.0031	97.955 7	0.003 1		
CENAMEP	99.079 0	0.001 4	97.950 0	0.001 5		
INDECOPI	99.076 9	0.003 5	97.952 3	0.003 5		
IBMETRO	99.083 3	0.001 7			100.931 3	0.001 7
LATU	99.083 1	0.0013			100.933 9	0.001 3
INTI	99.073 0	0.003 0			100.918 0	0.003 0
INMETRO	99.078 9	0.000 95			100.928 0	0.000 95
	RCRV [mL]	*U(RCRV)* [mL]	*RCRV* [mL]	*U(RCRV)* [mL]	*RCRV* [mL]	*U(RCRV)* [mL]
RCRV	**99.079 8**	**0.001 8**	**97.952 7**	**0.002 8**	**100.928 5**	**0.001 9**
Method	Median		Median		Median	

Due to the fact that the transfer standard 03.04.04 was the only one artifact tested by all of the participants, Degree of Equivalence $\boldsymbol{d_i}$, is computed using the results for 03.04.04 artifact.

When calculating the ***RCRV*** by the Cox method, denoted as *w-m*, several values were found to be discrepant. Attempts were made to resolve the inconsistency; however, after reviewing their calculations, no errors were found by the reviewers. Therefore, the median was selected as method for estimating the ***RCRV***, computed by means of the Monte Carlo Method. 20 000 trials were produced for generating the corresponding ***pdf***.

Appendix C contains details of the resultant ***RCRV*** pdf for volume of liquids at 100 mL, as produced by the Monte Carlo Method. The computation of degrees of equivalence $\boldsymbol{d_i}$ and its associated uncertainty $\boldsymbol{u(d_i)}$ has been computed also by Monte Carlo Method.

8. DETERMINATION OF THE DEGREES OF EQUIVALENCE, d_i

The ***RCRV*** for each artifact was determined according to the procedures suggested by Cox [14]. Appendix C shows the details on the calculation of the ***RCRV*** for each of the Transfer Standards. Tables 9 and 10 show a summary of the degrees of equivalence for the 20 L and 100 mL artifacts.

To calculate the degrees of equivalence d_i, between the RCRV and the corresponding NMIs, the following formula is used,

$$d_i = x_i - x_{ref} \qquad (1)$$

The uncertainty for d_i was computed using the assumed probability distribution from the 20 000 Monte Carlo trials. 2.5 % and 97.5 % limits were used to set the expanded uncertainty, $U(d_i)$.

Table 9 Degrees of equivalence d_i, for artifacts 710-05, Volume of Liquids at 20 L.

20 L TS	**710-05**		
	d_i	$U(d_i)$	E_i
	$\times 10^{-6}$		$= \lvert d_i/U(d_i) \rvert$
CENAM♦	7	30	0.23
NIST♦	45	61	0.74
BSJ	86	630	0.14
LACOMET	-225	147	1.53
CENAMEP	29	54	0.54
INDECOPI	-22	84	0.26
IBMETRO	-36	92	0.39
LATU	-70	63	1.11
INTI	7	25	0.28
INMETRO♦	8	29	0.28
Method	median		

Graph 1 Degrees of equivalence for artifact 710-05, volume at 20 L. ♦represents CCM.FF-K4 linking NMIs. Uncertainty bars are expressed with a coverage factor, $\boldsymbol{k}$=2.

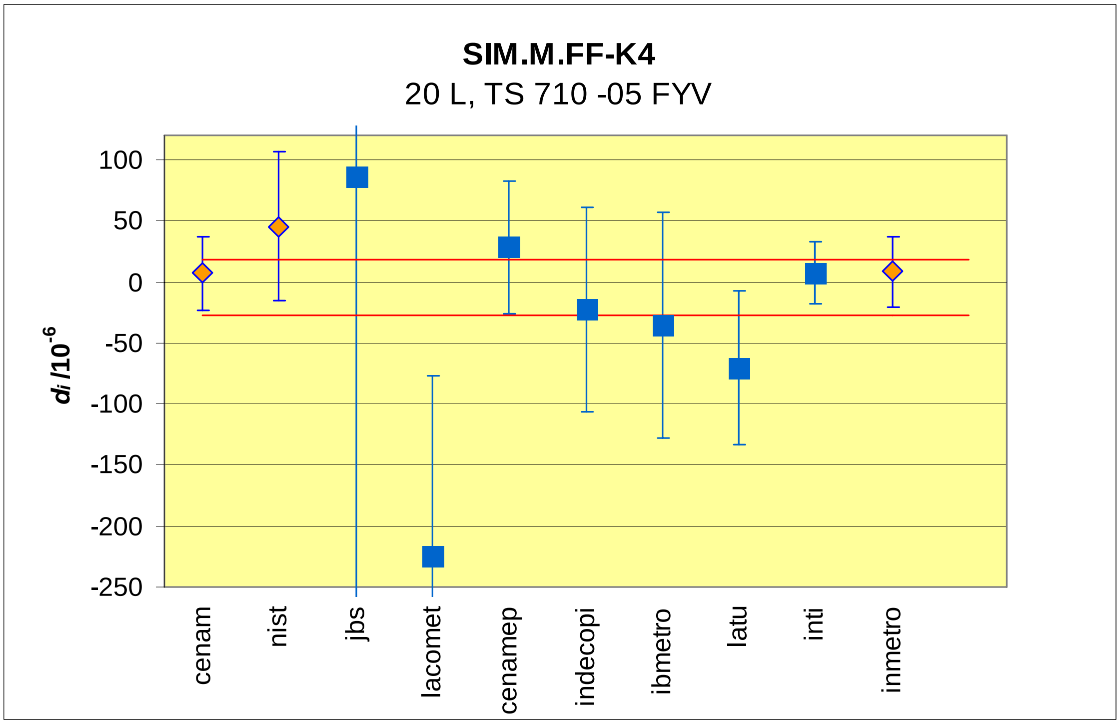


Table 10 Degrees of equivalence d_{ij}, for volume at 20 L.

20 L TSs		1		2		3		4		5		6		7		8		9		10	
		d_{ij}	$U(d_{ij})$																		
		$\times 10^{-6}$																			
1	CENAM			-38	64	-79	640	232	148	-22	59	29	92	42	100	77	67	-1	28	-1	34
2	NIST	38	64			-41	642	270	157	17	79	68	107	81	113	115	85	38	60	37	64
3	BSJ	79	640	41	642			311	657	58	641	109	645	122	647	156	642	79	640	78	640
4	LACOMET	-232	148	-270	157	-311	657			-253	154	-202	171	-189	173	-155	158	-232	146	-232	147
5	CENAMEP	22	59	-17	79	-58	641	253	154			51	103	64	110	98	80	21	54	20	58
6	INDECOPI	-29	92	-68	107	-109	645	202	171	-51	103			13	132	47	107	-30	90	-31	92
7	IBMETRO	-42	100	-81	113	-122	647	189	173	-64	110	-13	132			34	114	-43	97	-44	99
8	LATU	-77	67	-115	85	-156	642	155	158	-98	80	-47	107	-34	114			-77	62	-78	64
9	INTI	1	28	-38	60	-79	640	232	146	-21	54	30	90	43	97	77	62			-1	26
10	INMETRO	1	34	-37	64	-78	640	232	147	-20	58	31	92	44	99	78	64	1	26		

Table 11 Degrees of equivalence d_i, for artifact 03.04.04, Volume of liquids at 100 mL

100 mL TS	03.04.04		
	d_i	$U(d_i)$	E_i
	$\times 10^{-6}$		$= \lvert d_i/U(d_i) \rvert$
CENAM	4	39	0.1
BSJ	10 603	733	14.5
LACOMET	20	64	0.31
CENAMEP	-8	33	0.24
INDECOPI	-29	70	0.41
IBMETRO	35	37	0.95
LATU	33	32	1.03
INTI	-70	62	1.13
INMETRO	-10	26	0.38
Method	median		

Graph 2 Degrees of equivalence for artifact 03.04.04, volume at 100 mL. The red lines represent the 95 % uncertainty limits for the ***RCRV***.

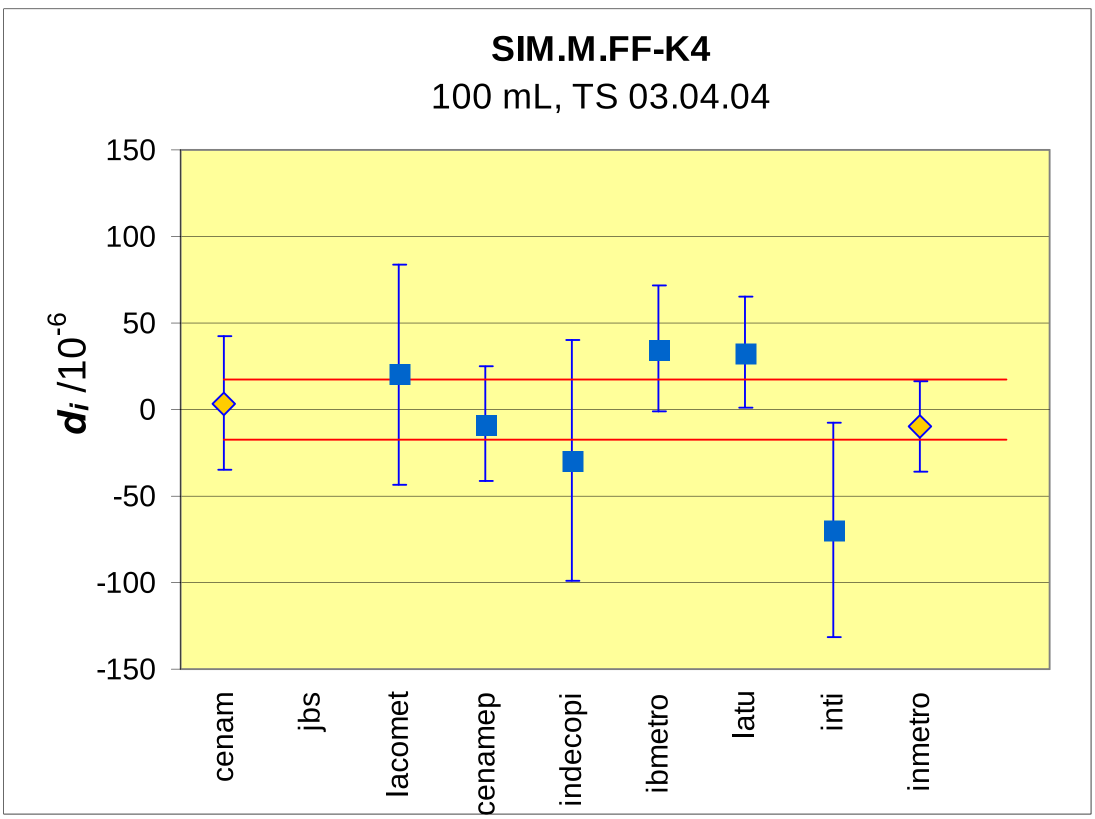


Table 12 Degrees of equivalence d_{ij}, for volume at 100 mL.

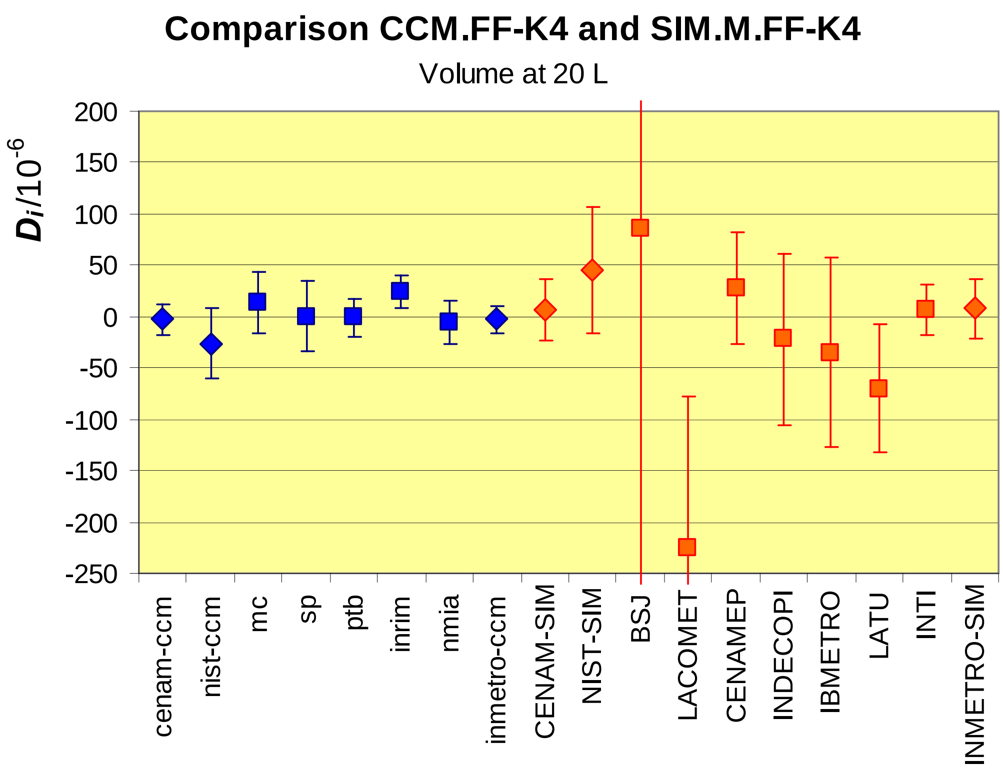
100 mL TS		**1**		**2**		3		4		5		6		7		8		9	
		d_{ij}	$U(d_{ij})$																
		$\times 10^{-6}$																	
1	CENAM			10550	735	-16	70	12	43	34	77	-31	47	-29	40	73	67	14	37
2	BSJ	-10550	735			10534	734	10562	732	10584	738	10519	734	10521	736	10622	735	10563	734
3	LACOMET	16	70	-10534	734			28	67	50	92	-15	71	-13	67	89	86	30	65
4	CENAMEP	-12	43	-10562	732	-28	67			22	75	-43	45	-41	38	60	66	1	35
5	INDECOPI	-34	77	-10584	738	-50	92	-22	75			-65	78	-63	74	39	91	-20	72
6	IBMETRO	31	47	-10519	734	15	71	43	45	65	78			2	42	104	69	45	39
7	LATU	29	40	-10521	736	13	67	41	38	63	74	-2	42			102	66	43	32
8	INTI	-73	67	-10622	735	-89	86	-60	66	-39	91	-104	69	-102	66			-59	63
9	INMETRO	-14	37	-10563	734	-30	65	-1	35	20	72	-45	39	-43	32	59	63		

9. Link to CCM.FF-K4

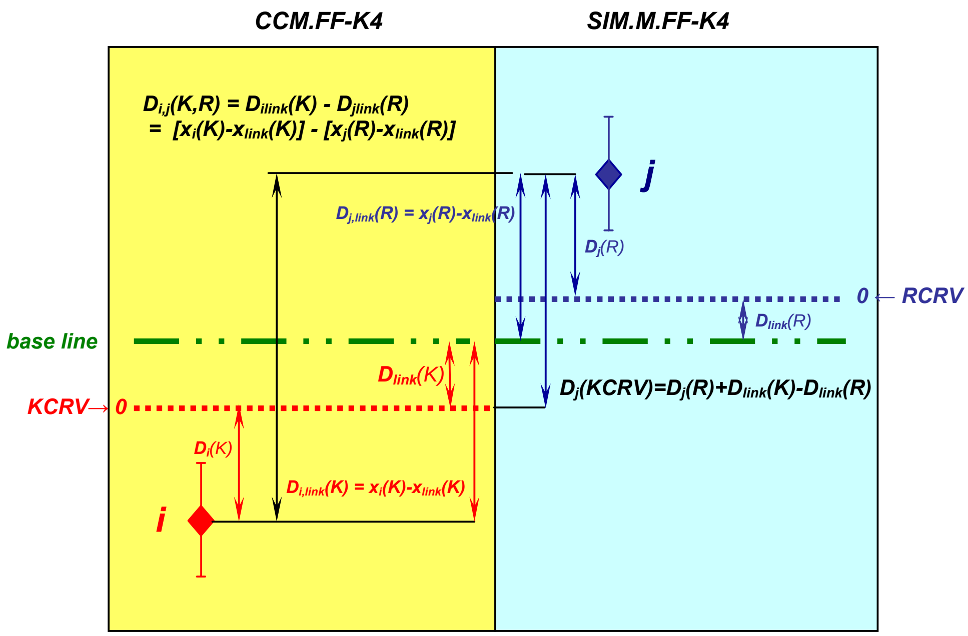
9.1 Volume at 20 L

The transfer standard 710-05FyV that circulated within the SIM 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 SIM: NIST (USA), INMETRO (Brazil) and CENAM (Mexico) re-measured the changed volume of this volume standard. The outcome of both comparisons is presented graphically in figure D1.

Graph 3 Degrees of Equivalence related to CCM.FF-K4 and SIM.M.FF-K4. ***DoE***s were calculated for the corresponding reference value (KCRV for CCM.FF-K4 and RCRV for SIM.M.FF-K4. Diamond marks corresponds to the linking NMIs.



Graph 4 Schematic diagram for the linking procedure for Volume of Liquids at 20 L and 100 mL.



Linking SIM results to CCM.FF-K4 ***KCRV*** and to any CCM.FF-K4 participant will require defining linking NMIs. As can be seen in Graph 4, the degree of equivalence of SIM participants to KCRV can be calculated as

$$\boldsymbol{D_j}(SIM,KCRV) = \boldsymbol{D_j}(RCRV)+\boldsymbol{D_{link}}(R) - \boldsymbol{D_{link}}(K) \quad (2)$$

where

$\boldsymbol{D_j(SIM,KCRV)}$:	Degree of equivalence for a SIM participant to CCM.FF-K4 ***KCRV***
$\boldsymbol{D_j(RCRV)}$:	Degree of equivalence for a SIM participant to the SIM.M.FF-K4 ***RCRV***. $= \boldsymbol{x_j - RCRV}$
$\boldsymbol{D_{link}(R)}$:	$= \boldsymbol{x_{link}(R)\text{-}RCRV}$
$\boldsymbol{D_{link}(K)}$:	$= \boldsymbol{x_{link}(K)\text{-}KCRV}$

$\boldsymbol{x_{link}(K)}$ and $\boldsymbol{x_{link}(R)}$ can be computed as the average ***DoEs*** for the linking participants (CENAM, NIST and INMETRO) at CCM.FF-K4 and SIM.M.FF-K4, respectively. However, due to the fact that NIST results are discrepant to the other two, CENAM and INMETRO serve as the linking results. CENAM and INMETRO are consistent to each other at approximately 95 % level of confidence.

When calculating the uncertainty for linking SIM results to ***KCRV*** and to the CCM.FF-K4 participants, a correlation coefficient equal to 1 is applied for $\boldsymbol{D_{link}(K)}$ ***and*** $\boldsymbol{D_{link}(R)}$.

Table 13 summarizes the SIM.M.FF-K4 linkage to CCM.FF-K4.**Table 13** SIM.M.FF-K4 linkage to CCM.FF-K4 for Volume of liquids at 20 L.

i ↓ *j* →	d_i	$U(d_i)$	CENAM (1)		2		3		4		5		6		7		8		9		10		11		12		13		14		15	
	$\cdot 10^{-6}$		d_{ij}	$U(d_{ij})$	$\cdot 10^{-6}$																											
CENAM	-3	22			-38	64	-79	640	232	148	-22	59	29	92	42	100	77	67	-1	28	-1	34	-22	37	-5	41	-6	29	-35	26	8	31
NIST	35	59	38	64			-41	642	270	157	17	79	68	107	81	113	115	85	38	60	37	64	16	67	33	70	31	63	3	61	45	63
BSJ	73	631	79	640	41	642			311	657	58	641	109	645	122	647	156	642	79	640	78	640	59	632	77	628	75	630	47	629	89	630
LACOMET	-235	145	-232	148	-270	157	-311	657			-253	154	-202	171	-189	173	-155	158	-232	146	-232	147	-255	147	-237	148	-239	145	-267	144	-225	145
CENAMEP	19	54	22	59	-17	79	-58	641	253	154			51	103	64	110	98	80	21	54	20	58	0	61	18	65	16	56	-13	55	30	57
INDECOPI	-33	89	-29	92	-68	107	-109	645	202	171	-51	103			13	132	47	107	-30	90	-31	92	-51	92	-34	94	-36	89	-64	88	-22	90
IBMETRO	-46	95	-42	100	-81	113	-122	647	189	173	-64	110	-13	132			34	114	-43	97	-44	99	-64	98	-47	101	-48	96	-77	95	-34	97
LATU	-80	59	-77	67	-115	85	-156	642	155	158	-98	80	-47	107	-34	114			-77	62	-78	64	-99	66	-81	68	-83	62	-112	60	-69	62
INTI	-3	19	1	28	-38	60	-79	640	232	146	-21	54	30	90	43	97	77	62			-1	26	-22	34	-5	38	-6	24	-34	20	8	26
INMETRO	-2	20	1	34	-37	64	-78	640	232	147	-20	58	31	92	44	99	78	64	1	26			-21	36	-3	40	-5	27	-33	24	9	28
MC	13	30	22	37	-16	67	-59	632	255	147	0	61	51	92	64	98	99	66	22	34	21	36			13	45	14	36	-11	34	18	37
SP	0	34	5	41	-33	70	-77	628	237	148	-18	65	34	94	47	101	81	68	5	38	3	40	-13	45			1	39	-24	38	5	40
PTB	-1	19	6	29	-31	63	-75	630	239	145	-16	56	36	89	48	96	83	62	6	24	5	27	-14	36	-1	39			-25	25	4	28
INRIM	24	16	35	26	-3	61	-47	629	267	144	13	55	64	88	77	95	112	60	34	20	33	24	11	34	24	38	25	25			29	26
NMIA	-5	21	-8	31	-45	63	-89	630	225	145	-30	57	22	90	34	97	69	62	-8	26	-9	28	-18	37	-5	40	-4	28	-29	26		

SIM.M.FF-K4

CCM.FF-K4

Linkage: CCM – SIM

Linkage: SIM – ***KCRV***

9.2 Volume at 100 mL

The transfer standard (serial number 03.04.04) that circulated within the SIM laboratories was one of six 100 mL pycnometers that were calibrated earlier by six laboratories from three regional metrology organizations SIM (America), APMP (East Asia and Australia), Euramet (Europe) in the CIPM Key comparison – CCM-FF.K4. Two laboratories from SIM: INMETRO (Brazil) and CENAM (Mexico) re-measured the changed volume of this volume standard. The outcome of both comparisons is presented graphically in Graph 5.

Graph 5 Degrees of Equivalence related to CCM.FF-K4 and SIM.M.FF-K4. ***DoE***s were calculated for the corresponding reference value (***KCRV*** for CCM.FF-K4 and ***RCRV*** for SIM.M.FF-K4. Diamond marks corresponds to the linking NMIs.

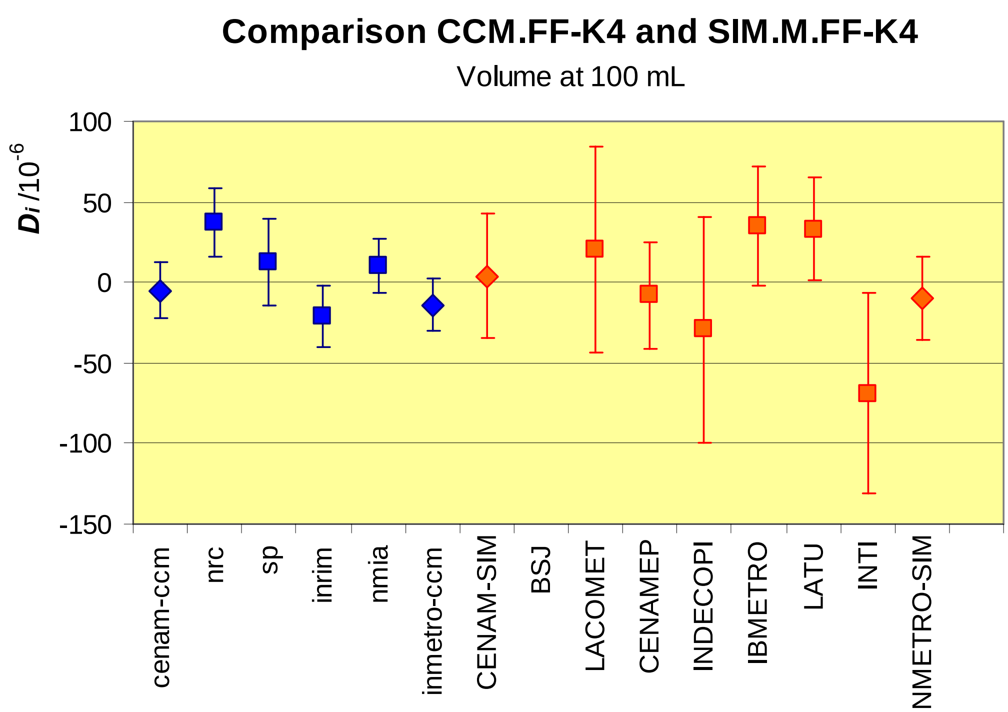


Table 14 SIM.M.FF-K4 linkage to CCM.FF-K4 for Volume of liquids at 100 mL.

i ↓ j →	d_i	$U(d_i)$	1		2		3		4		5		6		7		8		9		10		11		12		13	
	$\cdot 10^{-6}$		D_{ij}	$U(d_{ij})$																								
CENAM	-3	22			-10550	735	-16	70	12	43	34	77	-31	47	-29	40	73	67	14	37	-40	29	-16	40	18	30	-12	34
BSJ	10601	721	10550	735			10534	734	10562	732	10584	738	10519	734	10521	736	10622	735	10563	734	10510	730	10534	729	10568	731	10538	730
LACOMET	13	64	16	70	-10534	734			28	67	50	92	-15	71	-13	67	89	86	30	65	-24	64	0	69	35	64	4	65
CENAMEP	-15	32	-12	43	-10562	732	-28	67			22	75	-43	45	-41	38	60	66	1	35	-52	33	-28	43	6	34	-24	36
INDECOPI	-36	72	-34	77	-10584	738	-50	92	-22	75			-65	78	-63	74	39	91	-20	72	-74	71	-49	76	-15	71	-46	73
IBMETRO	28	38	31	47	-10519	734	15	71	43	45	65	78			2	42	104	69	45	39	-9	38	15	45	49	38	19	42
LATU	26	30	29	40	-10521	736	13	67	41	38	63	74	-2	42			102	66	43	32	-11	30	13	41	47	31	17	34
INTI	-75	63	-73	67	-10622	735	-89	86	-60	66	-39	91	-104	69	-102	66			-59	63	-113	61	-88	67	-54	62	-85	63
INMETRO	-16	22	-14	37	-10563	734	-30	65	-1	35	20	72	-45	39	-43	32	59	63			-54	24	-29	36	5	25	-26	29
NRC	37	21	40	29	-10510	730	24	64	52	33	74	71	9	38	11	30	113	61	54	24			25	34	51	28	30	27
SP	12	27	16	40	-10534	729	0	69	28	43	49	76	-15	45	-13	41	88	67	29	36	-25	34			26	33	5	32
INRIM	-14	19	-18	30	-10568	731	-35	64	-6	34	15	71	-49	38	-47	31	54	62	-5	25	-51	28	-26	33			-21	25
NMIA	7	17	12	34	-10538	730	-4	65	24	36	46	73	-19	42	-17	34	85	63	26	29	-30	27	-5	32	21	25		

SIM.M.FF-K4

CCM.FF-K4

Linkage: CCM – SIM

Linkage: SIM – ***KCRV***

10.- DISCUSSION OF RESULTS

Objective of the comparison

The main objective of the project was to compare the extent of comparability within participating NMIs in performing determinations of volume of water. By using transfer standards of excellent metrological characteristics, what actually was compared is the ability of: producing and maintaining pure water, using proper equation of state for water, determining the mass of water, correcting volume from actual to reference conditions, mainly. In this sense, despite the wide range of methods employed, the overall agreement is found to be in the order of $\pm 70 \cdot 10^{-6}$.

Degrees of equivalence

Looking at the 20 L measurements, the majority of the d_i results overlap among them; it is however noticeable that $d_{LACOMET}$ barely overlaps with three NMIs. Two SIM laboratories, out of ten, do not overlap the ***RCRV*** or the ***KCRV***.

As for the 100 mL results, it is noticeable that BSJ data is inconsistent with all others; not just for 03.04.04 artifact, but also for 03.01.15; which can be interpreted as experimental error. Two laboratories, out of nine, do not overlap the ***RCRV*** or the ***KCRV***.

Uncertainty claims

According to the uncertainty analysis provided by each participant, the three major sources of uncertainty are related to: 1) water density and temperature (the correlation of the two), 2) repeatability of the measurements and 3) mass determination.

In average, the variance associated to type B contributions is about 15 times the variance associated to type A contributions; somehow, this fact reflects that some participants tend to overestimate type B contributions.

Despite the Technical Protocol including an uncertainty calculation format, it is evident that there is a need to produce a Technical Guide for Uncertainty Calculations for Volume of Liquids Measurements within SIM NMIs.

11. CONCLUSIONS

- The used transfer standards for SIM.M.FF-K4 exhibited good performance all way long, both: in terms of stability and repeatability; however, one out of two transfer standards for 100 mL was broken during transportation.
- Degrees of equivalence d_i have been produced by using the data for artifact 710-05 for volume at 20 L and data for artifact 03.04.04 for volume at 100 mL.
- The best estimation of the measurands, as reported by the participants, show a general agreement better than ± 0.007 0 % for volume of liquids at 100 mL and 20 L.
- It is advisable to review the uncertainty analysis of some participants.

- New CMC entries for some NMIs should take into account the information presented herein.

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Appendix A
-Figures -

Fig. 1 Photograph of the assembled transfer standard.

Fig. 2 An image of the Gay-Lussac type pycnometers for volumes of 100 mL

APPENDIX B (traceability information)

Table A.1 Traceability information for measurements at 20 L. Values in blue (and shaded) represent standard uncertainty for the corresponding quantity.

20 L	BALANCE	WEIGHTS	THERMOMETER	PRESSURE	RELATIVE HUMIDITY METER	TRACEABILITY
CENAM	Mettler KB60 60 kg/0.01 g/0.090 g	Rice Lake E2, Masstech F1	Liquid in glass Brooklin, 15 mK	Barometer Druck DPI 740 2 Pa	Capacitive Vaisala HM34 0.7 %	CENAM
NIST	Mettler PK60 60 kg/0.01 g/0.3 g	Rice Lake 1 ppm	Hart Chub E4 0.3 ºC	Vaisala PTV200 150 Pa	Vaisala PTV200 2.5 %	NIST
BSJ	N/A	N/A	Omega HH22	N/A	N/A	PTB
LACOMET	Mettler ID7 50 kg/5 mg/5mg	Sartorius F1	Cole Palmer 3313-65 0.01 ºC	Cole Palmer 3313-65 50 Pa	Cole Palmer 3313-65 1 %	LACOMET
CENAMEP	Mettler Toledo KA30 30 kg/5 mg/0.058 mg	Häfner F1	Control Company 1870 1 ºC	Control Company 1870 1 hPa	Control Company 1870 1 %	CENAMEP/mass LACOMET/p, t, hr
INDECOPI	Mettler Toledo 32 kg/0.1 g/0.22 g	Mettler F1, E2	LUFFT 0.175 ºC	Richard – Pekly 20 Pa	LUFFT 1.6 %	PTB CENAM/p
IBMETRO	Sauter 50 kg/10 mg/5 mg	Troemmer, Sartorius, E2	ALMEMO 6290-7 0.15 ºC	LUFT OPUS II 46 Pa	ALMEMO 6290-7 1.5 %	IBMETRO
LATU	Sartorius 30 kg/0.1 g/0.23 g	Sartorius F1	Testo 0.25 ºC	Testo 200 Pa	Testo 3 %	PTB/m LATU, INTI/p,t, hr
INTI	Sauter 50 kg/10 mg/10 mg	Doltz F1	Film Pt-100 0.05 ºC	Paroscientific 15 Pa	TECMES 2 %	INTI
INMETRO	Sartorius C60000 60 kg/0.1 g	Häfner F1 /7 mg	Thermoschneider 0.03 ºC	Oregon Scientific BAR 928 / 20 Pa	Oregon Scientific BAR 928 / 1.1 %	INMETRO

Table A.2 Traceability information for measurements at 100 mL. Values in blue (and shaded) represent standard uncertainty for the corresponding quantity.

100 mL	BALANCE	WEIGHTS	THERMOMETER	PRESSURE	RELATIVE HUMIDITY METER	TRACEABILITY
CENAM	Sartorius 210 g/0.01 mg/0.08 mg		Liquid in glass Brooklin, 15 mK	Barometer Druck DPI 740 2 Pa	Capacitive Vaisala HM34 0.7 %	CENAM
BSJ	N/A 5.7 mg	N/A	Omega HH22 0.025 ºC	N/A 120 Pa	N/A 5 %	PTB
LACOMET	Mettler AT201 200 g/0.1 mg/0.1 mg	Sartorius E2	Vaisala PTU200 0.1 ºC	Vaisala PTU200 7 Pa	Vaisala PTU200 1.5 %	LACOMET Vaisala
CENAMEP	Mettler Toledo AB2C4 210 g/0.1 mg/2.5 mg	Häfner F1 /0.75 mg	Control Company 1870 1 ºC	Control Company 1870 1 hPa	Control Company 1870 1 %	CENAMEP LACOMET/p,t,hr
INDECOPI	Mettler Toledo 220 g/0.1 mg/0.2 mg	Mettler E2	LUFFT 0.175 ºC	Richard – Pekly 20 Pa	LUFFT 1.6 %	PTB, CENAM/p
IBMETRO	Sartorius BP221S 50 kg/0.1 mg/0.1 mg	Kern, E2	LUFT OPUS II 0.36 ºC	LUFT OPUS II 46 Pa	LUFT OPUS II 1.03 %	IBMETRO
LATU	Mettler AG004 200 g/0.1 mg/0.31 mg	Mettler E2	Testo 0.25 ºC	Testo 200 Pa	Testo 3 %	PTB/m LATU, INTI/p,t, hr
INTI	Sartorius MC210S 210 g/0.01 mg/0.03 mg	Doltz E2	Film Pt-100 0.05 ºC	Paroscientific 15 Pa	TECMES 2 %	INTI
INMETRO	Sartorius ME215S 210 g/0.01 mg/0.04 mg		Thermoschneider 0.03 ºC	Oregon Scientific BAR 928 / 20 Pa	Oregon Scientific BAR 928 / 1.1 %	INMETRO

APPENDIX B (uncertainty information)

Table B.1 Uncertainty contributions (in mL) to the uncertainty of the measurand at 20 L. Yellow shaded values (**Y**) represent the major source of uncertainty; whereas blue shaded values (**B**) the second largest contribution.

20 L TS - contributions in mL -	1	2	3	4	5	6	7	8	9	10
Balance	0.021	0.42		0.011	0.56	0.17		0.225	0.017	
Weights	0.042				0.017	0.026				0.022
water temperature (calibration)	0.056	0.13	0.01	0.005	0.12				0.06	0.015
Temperature gradients					0.45				0.06	
water density	0.24	0.20		0.17		0.602			0.01	0.17
air temperature	0.016	0.04		0.014	0.0002	0.063			0.02	6.6e-05
Ambient pressure										5.7e-5
Relative humidity										0.0028
Artifact temperature						0.079			0.014	0.0048
Thermal expansion coefficient	0.003	0.01	0.01	0.02	0.01	0.02			0.002	2.6e-4
Leaks										
Evaporation						0.58				
Clingage								0.3		
Repeatability	0.036	0.33	6.43	0.85	0.087	0.19	0.068	0.20	0.071	0.12
Others	0.029			1.25*			0.95	0.4		
combined uncertainty; [mL]	0.25	0.59	6.44	1.46	0.53	0.89	0.96	0.59	0.12	0.23
expanded uncertainty; [mL]	**0.54**	**1.32**	**12.87**	**2.92**	**1.5**	**1.8**	**1.93**	**1.18**	**0.25**	**0.47**

1: cenam, 2: nist, 3: bsj, 4:lacomet, 5:cenamep, 6:indecopi, 7:ibmetro, 8:latu, 9:inti, 10:inmetro
* reproducibility

Table B.2 Uncertainty contributions (in µL) to the uncertainty of the measurand at 100 mL. Yellow shaded values (**Y**) represent the major source of uncertainty; whereas blue shaded values (**B**) the second largest contribution.

<table>
<tr><th>100 mL TS
- contributions in µL</th><th>1</th><th>2</th><th>3</th><th>4</th><th>5</th><th>6</th><th>7</th><th>8</th><th>9</th></tr>
<tr><td>Balance</td><td>0.084</td><td rowspan="2">5.0</td><td>0.14</td><td>1.324</td><td>0.189</td><td></td><td></td><td>0.223</td><td>0.032</td></tr>
<tr><td>Weights</td><td>0.204</td><td>0.065</td><td>0.085</td><td>0.126</td><td></td><td></td><td>0.240</td><td>0.11</td></tr>
<tr><td>water temperature (calibration)</td><td rowspan="2">1.237</td><td rowspan="2">0.025</td><td rowspan="2">0.007</td><td rowspan="2">0.063</td><td>0.071</td><td></td><td></td><td></td><td>0.008</td></tr>
<tr><td>Temperature gradients</td><td rowspan="2">2.982</td><td></td><td></td><td>2.800</td><td></td></tr>
<tr><td>water density</td><td>0.041</td><td>2.5</td><td>0.15</td><td>0.437</td><td></td><td></td><td>0.050</td><td>0.81</td></tr>
<tr><td>air temperature</td><td>0.044</td><td rowspan="3">0.023</td><td rowspan="3">0.053</td><td rowspan="3">0.5e-3</td><td rowspan="3">0.313</td><td rowspan="3"></td><td></td><td>0.24e-3</td><td rowspan="3">0.33</td></tr>
<tr><td>Ambient pressure</td><td>0.021</td><td></td><td>0.35e-3</td></tr>
<tr><td>Relative humidity</td><td>0.007</td><td></td><td>0.23e-3</td></tr>
<tr><td>Artifact temperature</td><td>0.11</td><td></td><td></td><td></td><td>0.071</td><td></td><td></td><td>0.140</td><td>5e-3</td></tr>
<tr><td>Thermal expansion coefficient</td><td>0.4e-4</td><td>0.738</td><td>0.1</td><td></td><td>0.039</td><td></td><td></td><td>1e-3</td><td>0.25e-3</td></tr>
<tr><td>Leaks</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Evaporation</td><td>0.13</td><td></td><td></td><td></td><td>1.155</td><td></td><td></td><td>0.397</td><td></td></tr>
<tr><td>Clingage</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Repeatability</td><td>0.59</td><td></td><td>2.73</td><td>0.074</td><td>0.520</td><td>1.546</td><td>0.172</td><td>0.300</td><td>0.29</td></tr>
<tr><td>Others</td><td>0.78*</td><td>36.6**</td><td></td><td></td><td></td><td>0.707</td><td>1.238</td><td>0.050</td><td>0.21</td></tr>
<tr><td>combined uncertainty; [µL]</td><td>1.60</td><td>37</td><td>3.1</td><td>1.4</td><td>3.5</td><td>1.7</td><td>1.25</td><td>3.0</td><td>0.95</td></tr>
<tr><td>expanded uncertainty; [µL]</td><td>3.2</td><td>74</td><td>6.2</td><td>3.0</td><td>7.0</td><td>3.4</td><td>2.5</td><td>6.0</td><td>1.9</td></tr>
</table>

1: cenam, 2: jbs, 3:lacomet, 4:cenamep, 5:indecopi, 6:ibmetro, 7:latu, 8:inti, 9:inmetro

* reproducibility (metrologist effect)

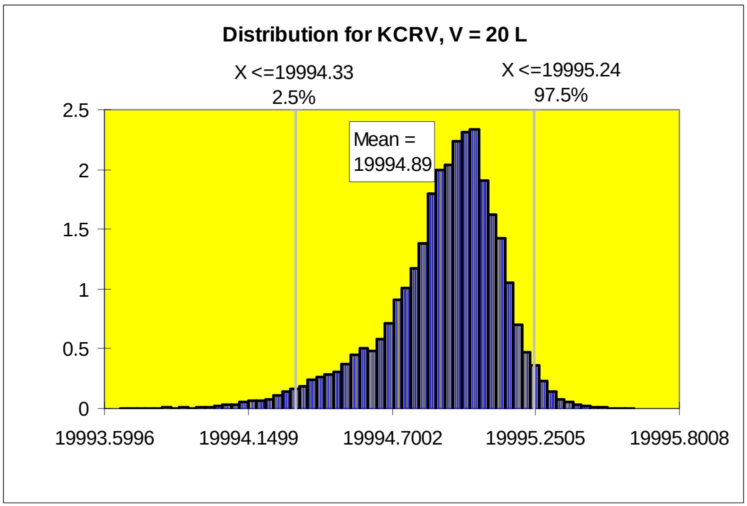
** contribution due to the method

APPENDIX C

C.1 Computation of the *RCRV* for **TS 710-05**, volume at 20 L.

First step: Performing consistency check using all results

Volume at 20 L		x_i [mL]	$u(x_i)$ [mL]	$x_i/u(x_i)^2$	$1/u(x_i)^2$	$(x_i-x_{ref})^2/u^2(x_i)$
1	CENAM	19995.03	0.25	319920.48	16	0.027781231
2	NIST	19995.79	0.59	57442.66016	2.872737719	1.846232682
3	JBS	19996.62	6.40	488.1987793	0.024414063	0.065158087
4	LACOMET	19990.39	1.46	9378.115031	0.469131169	9.919612323
5	CENAMEP	19995.47	0.53	71183.58847	3.55998576	0.825935466
6	INDECOPI	19994.45	0.89	25242.33051	1.26246686	0.365862883
7	IBMETRO	19994.18	0.96	21695.07378	1.085069444	0.708982846
8	LATU	19993.50	0.59	57436.08159	2.872737719	6.487231516
9	INTI	19995.04	0.12	1388544.444	69.44444444	0.18539667
10	INMETRO	19995.06	0.23	377978.4499	18.90359168	0.097097964
			$\sum$	2329309.423	116.4945789	20.3813805
			RCRV (x_{ref})		19995.003	
			u(RCRV)		0.093	
			ν			
TS 710-05			χ^2_{obs}			
			$\Pr\{\chi^2(\nu) > \chi^2_{obs}\}$		**1.57 %**	



Minimum	19993.66
Mean	**19994.89**
Maximum	19995.62
Std Dev	**0.2256049**
Variance	5.089756E-02
Skewness	-0.968586
Kurtosis	4.446339
Mode	19995
Left X	19994.33
Left P	2.5%
Right X	19995.24
Right P	97.5%
Diff. X	0.9121094
Diff. P	95%

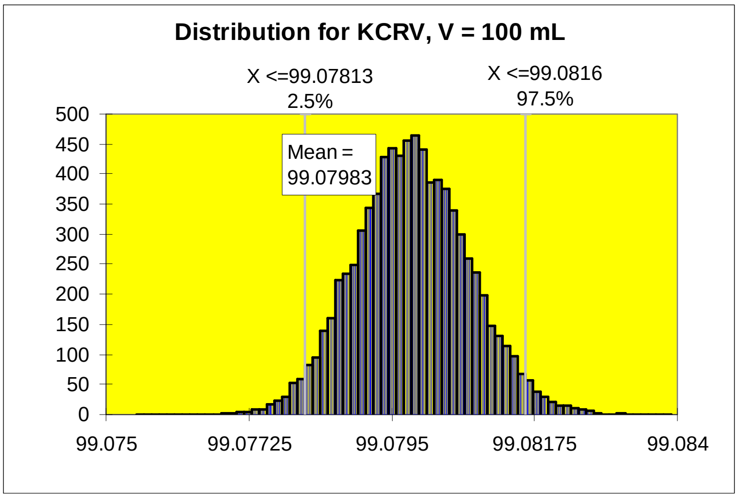
Fig. 1 Calculation results for ***RCRV*** for volume at 20 L by Monte Carlo Method. 20 000 trials were used to compute ***RCRV***, $\boldsymbol{d_i}$, $\boldsymbol{d_{ij}}$, $\boldsymbol{u(d_i)}$ and $\boldsymbol{u(d_{ij})}$.

C.2 Computation of the *RCRV* for **TS 03.04.04,** volume at 100 mL.

First step: Performing consistency check using all results

Volume at 100 mL		x_i [mL]	$u(x_i)$ [mL]	$x_i/u(x_i)^2$	$1/u(x_i)^2$	$(x_i-x_{ref})^2/u^2(x_i)$
1	CENAM	99.0802	0.00160	38703203.13	390625	0.166075742
2	JBS	100.1307	0.03700	73141.49014	730.4601899	807.1005168
3	LACOMET	99.0818	0.00310	10310280.96	104058.2726	0.527749881
4	CENAMEP	99.0790	0.00140	50550510.2	510204.0816	0.15319493
5	INDECOPI	99.0769	0.00350	8087910.204	81632.65306	0.572383783
6	IBMETRO	99.0833	0.00170	34284878.89	346020.7612	4.87120801
7	LATU	99.0831	0.00125	63413184	640000	8.07486454
8	INTI	99.0730	0.00300	11008111.11	111111.1111	4.763978097
9	INMETRO	99.0789	0.00044	511770919.4	5165289.256	2.516273668

	Σ	728202139.4	7349671.596	828.7462455
	$RCRV\ (x_{ref})$		99.079548 mL	
	$u(RCRV)$		0.00037 mL	
	ν		8	
TS 03.04.04	χ^2_{obs}		828.7462455	
	$\Pr\{\chi^2(\nu) > \chi^2_{obs}\}$		0.000	



Minimum	99.07549
Mean	**99.07983**
Maximum	99.08389
Std Dev	**8.898551E-04**
Variance	7.918421E-07
Skewness	0.1044233
Kurtosis	3.053223
Mode	99.07979
Left X	99.07813
Left P	2.5%
Right X	99.0816
Right P	97.5%
Diff. X	3.479004E-03
Diff. P	95%

Fig. 2 Calculation results for RCRV for volume at 100 mL by Monte Carlo Method. 20 000 trials were used to compute ***RCRV***, $\boldsymbol{d_i}$, $\boldsymbol{d_{ij}}$, $\boldsymbol{u(d_i)}$ and $\boldsymbol{u(d_{ij})}$.