BIPM/CIPM key comparison CCM.FF-K4.1.2011

Final Report
for
Volume of Liquids at 20 L and 100 mL

- Piloted by Centro Nacional de Metrología (**CENAM)**

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CONTENT

1. INTRODUCTION

During the 10th WGFF meeting, held in Taiwan in October 2010, it was agreed to perform the second round of CCM.FF-K4 for Volume of Liquids at 20 L and 100 mL. CENAM offered to act as the pilot laboratory; and started re-manufacturing the TSs for the intended purpose. Based on comments from volume technical experts that participated in the first version of this KC, some improvements were implemented on the TSs, so that better repeatability and reproducibility were expected for CCM.FF-K4.1.2011.

2. CONDITIONS SELECTED

Each laboratory was responsible for receiving the Transfer Packages, testing and sending them to the next participant according to the schedule –see section 3–.

The participating laboratories determined the volume of water that each of the two Transfer Standards (TS) of 20 L 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 three 100 mL TSs –glass pycnometers of the Gay-Lussac type– is able to **contain,** at a reference temperature of 20 °C.

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

When the standards arrived at the participating laboratory, a visual inspection of the outer and inner surfaces was made and the results noted on the corresponding formats. CENAM, as the pilot laboratory, received information about the arrival and departure dates and about the results of the visual inspection.

The pilot laboratory collected and analyzed the results. This report will be published in the CIPM Key Comparison Data Base.

3. PARTICIPANTS AND SCHEDULE

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

#	NMI	Date	Contact	Remarks
1	CENAM, México	03/2012	Roberto Arias rarias@cenam.mx	Pilot
2	NIST, USA	05/2012	John Wright john.wright@nist.gov	SIM participant
3	IPQ, Portugal	07/2012	Elsa Batista ebatista@ipq.pt	EURAMET participant
4	VSL, Netherlands	08/2012	Erik Smits fsmits@vsl.nl	EURAMET participant
5	SP, Sweden	09/2012	Olle Penttinen Olle.Penttinen@sp.se	EURAMET
6	INRIM, Italy	10/2012	Andrea Malengo a.malengo@inrim.it	EURAMET pivot
7	NIM, China	01/2013	Wang Jintao Wangjt@nim.ac.cn	APMP pivot
8	KEBS, Kenya	04/2013	Dominic Ondoro ondorodom@kebs.org	AFRIMET participant
9	INMETRO, Brazil	02/2014	Dalni Malta dsfilho@inmetro.gov.br	SIM participant

In June 2013, KEBS ordered the shipping of the TSs to INMETRO by using Kenyan Airways Cargo Services; however, due to the fact that the consignee was not INMETRO but INMETRO´s Technical Contact, it took 8 months to clear Brazilian customs; this fact affected the overall progress of the comparison. Fortunately, the TSs did not show damage after such a long waiting period at the Brazilian customs.

4. THE TRANSFER PACKAGES

4.1 Transfer Package for 20 L (two items)

Each transfer standard (TS) consists of: a) the 20 L pipette, b) a hand held digital thermometer, c) fittings for assembling and disassembling.

The 20 L pipette (see Fig. 6), which is made of stainless steel, has been designed to:

a) Minimize the contribution of the meniscus reading to the volume uncertainty,
b) Minimize the quantity of water drops attained to the inner surface after drainage.
c) Provide a leak-free metal to metal seal between the two parts of the container,
d) Minimize the risk of volume changes, and
e) 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.

Based on experience and on reference data, CENAM, as the Pilot Laboratory, selected $(47.7 \pm 2.0)\times10^{-6}$ $°C^{-1}$ as the cubic coefficient of expansion for the stainless steel used to make the TS; uncertainty is expressed as standard uncertainty.

4.2 Transfer Package for 100 mL (three items)

The Transfer Standards for volume at 100 mL are commercially available glass pycnometers (Gay Lussac Type, see Fig. 7). Made out of boro-silicate glass, they were manufactured according to ISO 3507.

A set of three 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 is provided by the manufacturer as 3.3×10^{-6} $°C^{-1}$; this value is transformed to a cubic expansion coefficient of $(9.9 \pm 1)\times10^{-6}$ $°C^{-1}$.

5. MEASUREMENT PROGRAM

Each participating laboratory tested each transfer standard so that 10 measurements were performed for each artifact. Table 1 shows an example of the testing program.

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

<table>
<tr><td colspan="2" rowspan="2"></td><th colspan="5">Date of test</th></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td></tr>
<tr><th rowspan="5">Measurements per day</th><td>1</td><td rowspan="5">Reception and inspection</td><td rowspan="5">Experimental set-up and Acclimatization</td><td>x_1</td><td>x_6</td><td rowspan="5">Packaging of the TS´s for shipment to next NMI.</td></tr>
<tr><td>2</td><td>x_2</td><td>x_7</td></tr>
<tr><td>3</td><td></td><td></td></tr>
<tr><td>4</td><td></td><td></td></tr>
<tr><td>5</td><td>x_5</td><td>x_{10}</td></tr>
<tr><td colspan="3"></td><td colspan="4">$\bar{x} = \frac{1}{10}\sum x_i$
x_i are individual results referenced to 20° C.</td></tr>
</table>

6. EXPERIMENTAL PROCEDURES

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

	Weighing*		**Water****	**De-aerated water?**	**Density formula**
	20 L	100 mL			
CENAM	DS	DR	IE + O	No	Tanaka et al
NIST	DR		O	No	Patterson & Morris
IPQ	SS	SS	IE + O	No	Tanaka et al
VSL	DS	DS	DM+2D	No	Bettin & Spieweck
SP	DS	SS	IE	Yes	Bettin & Spieweck
INRIM	SS	SS	IE + 2D	No	Tanaka et al
NIM	ABA	SS	IE	No	Tanaka et al
INMETRO	ABA	DR	DI	No	measured

***Weighing:** *DS*: Double substitution; *DR*: direct reading; *SS*: single substitution; *ABA*: substitution weighing
****water:** IE: Ion exchange; O: Inverse osmosis; 1D: single distillation; 2D: double distillation, DM: demineralized

Appendix A and B include 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 pycnometers while being partially submerged in 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 participants.

Table 4. Summary of the thermal stability within the laboratories. $t_d - 20$ represents the difference between the temperature of the device under test (three 20 L TSs) and the reference temperature. $t_w - t_a$ represents the difference between water and ambient temperature.

Measurements at 20 L	CENAM	NIST	IPQ	VSL	SP	INRIM	NIM	INMETRO
$(t_d - 20)$/°C	–0.8	2.2	2.0	1.6	0.07	–0.11	–0.94	0.06
$(t_w - t_a)$/°C	–0.6	1.8	–0.21	–0.51	–0.77	–0.05	–0.66	–0.28

Kenya Bureau of Standards (KEBS), did not follow MRA rules in regards to the timelines for sending complete measurement results to the pilot laboratory; as consequence, and following the decision taken at the CCM-WGFF meeting in Paris, its measurement results are not taken into account for computing KCRV nor DoE, and are included in Appendix C. KEBS is encouraged to participate in a subsequent RMO KC for Volume of Liquids for CMC supporting issues.

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 measurement results of CENAM and are taken for the calculation of the KCRV.

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

20 L	date	initial	date	final	$\lvert\Delta V\rvert$/mL
		$(x_i \pm u(x_i))$/mL, $k = 2$		$(x_i \pm u(x_i))$/mL, $k = 2$	
TS 710-04	03/2012	19 990.75 ± 0.80	06/2014	19 990.76 ± 0.80	0.01
TS 710-05		19 993.50 ± 0.80		19 993.41 ± 0.80	0.09

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

100 mL	date	initial	date	final	$\lvert\Delta V\rvert$/mL
		$(x_i \pm u(x_i))$/mL, $k = 2$		$(x_i \pm u(x_i))$/mL, $k = 2$	
TS 03.01.12	03/2012	99.642 0 ± 0.002 6	06/2014	99.643 6 ± 0.002 6	0.001 6
TS 03.01.16		103.090 8 ± 0.002 6		103.092 5 ± 0.002 6	0.001 7
TS 03.01.17		100.596 8 ± 0.002 6		100.596 9 ± 0.002 6	0.000 1

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

It is to be noted that NIST did not test the 100 mL artifacts, the technical contact noted that they are not including calibration services of glassware in their corresponding CMC list. Therefore, 20 L TSs were tested by 8 participants, whereas 100 mL TSs by 7 NMIs.

7.2 Results reported by the participants

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

Table 7. Reported results for 20 L TSs.

20 L TSs	**TS 710-04**		**TS 710-05**	
	x_i/mL	$u(x_i)$/mL	x_i/mL	$u(x_i)$/mL
CENAM	19 990.75	0.40	19 993.50	0.40
NIST	19 990.92	0.58	19 993.39	0.58
IPQ	19 990.69	0.85	19 992.97	0.69
VSL	19 990.53	0.34	19 993.25	0.34
SP	19 990.62	0.25	19 993.45	0.25
INRIM	19 990.73	0.19	19 993.55	0.19
NIM	19 990.45	0.30	19 993.14	0.30
INMETRO	19 991.05	0.20	19 993.81	0.20

Table 8. Reported results for 100 mL TSs.

100 mL TSs	TS 03.01.12		TS 03.01.16		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	99.642 0	0.001 3	103.090 8	0.001 3	100.596 8	0.001 3
IPQ	99.643 8	0.000 77	103.092 0	0.000 8	100.597 3	0.000 8
VSL	99.643 9	0.001 9	103.091 9	0.001 9	100.595 4	0.001 9
SP	99.644 7	0.001 5	103.094 0	0.001 5	100.597 5	0.001 7
INRIM	99.643 6	0.000 83	103.092 1	0.000 83	100.595 7	0.000 83
NIM	99.639 1	0.001 4	103.091 1	0.001 1	100.593 8	0.001 7
INMETRO	99.643 3	0.000 48	103.091 9	0.000 46	100.595 5	0.000 44

8. COMPUTATION OF THE KEY COMPARISON REFERENCE VALUES

The KCRV for volume of liquids at 20 L and 100 mL has been calculated by applying the ***"weighted mean"*** method as suggested by Cox [13]. Tables 9 – 13 show the calculations.

Table 9. Consistency check and computation of KCRV for TS 710-04.

TS 710-04	x_i/mL	$u(x_i)$/mL	$x_i/u(x_i)^2$	$1/u(x_i)^2$	$(x_i - x_{ref})^2/u(x_i)^2$
CENAM	19 990.75	0.40	124 942.165	6.25	0.000
NIST	19 990.92	0.58	59 426.039	2.972 651 61	0.088
IPQ	19 990.69	0.85	27 668.779	1.384 083 04	0.004
VSL	19 990.53	0.34	172 928.464	8.650 519 03	0.409
SP	19 990.62	0.25	319 849.889	16	0.270
INRIM	19 990.73	0.19	553 759.751	27.700 831	0.012
NIM	19 990.45	0.30	222 116.098	11.111 111 1	0.994
INMETRO	19 991.05	0.20	499 776.137	25	2.213
		Σ	1980467.32	99.069 195 8	3.990
			x_{ref}/mL	19990.75	$\chi^2_{0.05,7}$ = 14.07
			$u(x_{ref})$/mL	0.10	pass

Figure 1. Measurement results for TS 710-04. Horizontal solid bold line represents the KCRV, calculated according to Cox method. Uncertainties are expressed at k = 2.

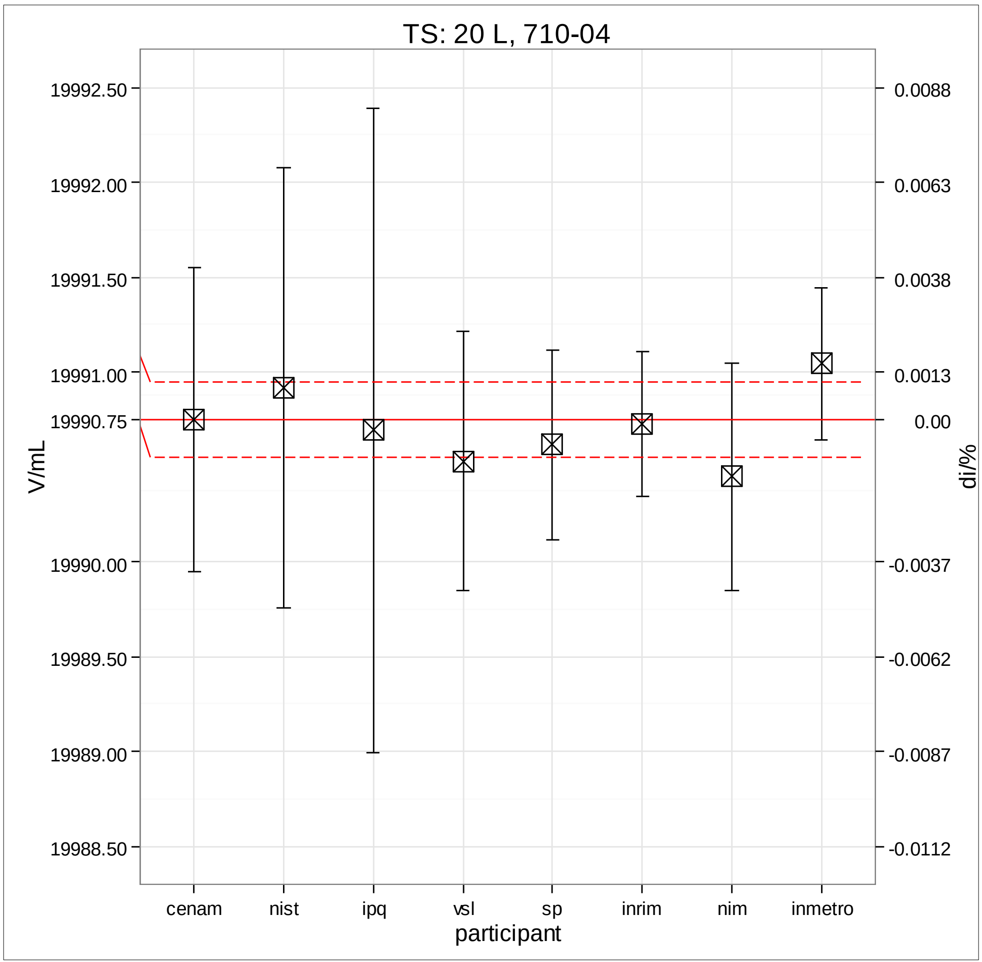


Table 10. Consistency check and computation of KCRV for TS 710-05.

TS 710-05	x_i/mL	$u(x_i)$/mL	$x_i/u(x_i)^2$	$1/u(x_i)^2$	$(x_i - x_{ref})^2/u(x_i)^2$
CENAM	19 993.50	0.40	124 959.401	6.25	0.005
NIST	19 993.39	0.58	59 433.371	2.972 651 61	0.064
IPQ	19 992.97	0.69	41 993.209	2.100 399 08	0.672
VSL	19 993.25	0.34	172 951.948	8.650 519 03	0.714
SP	19 993.45	0.25	319 895.179	16	0.112
INRIM	19 993.55	0.19	553 837.95	27.700 831	0.009
NIM	19 993.14	0.3	222 146.033	11.111 111 1	1.685
INMETRO	19 993.81	0.17	691 827.2	34.602 076 1	2.590
		Σ	2187044.29	109.387588	5.851
			x_{ref}/mL	19 993.53	$\chi^2_{0.05,7}$ = 14.07
			$u(x_{ref})$/mL	0.096	pass

Figure 2. Measurement results for TS 710-05. Horizontal solid bold line represents the KCRV, calculated according to Cox method. Uncertainties are expressed at k = 2.

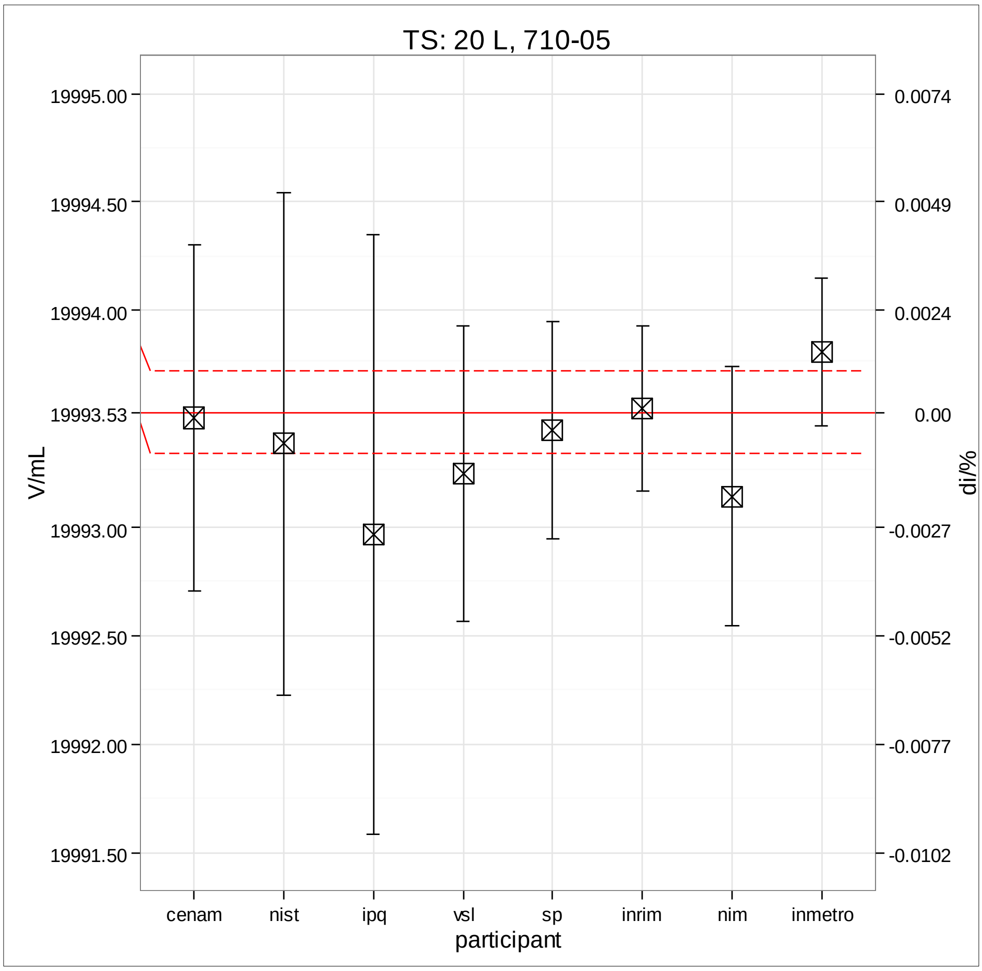


Table 11. Consistency check and computation of KCRV for TS 03.01.12.

TS 03.01.12	x_i/mL	$u(x_i)$/mL	$x_i/u(x_i)^2$	$1/u(x_i)^2$	$(x_i - x_{\mathrm{ref}})^2/u(x_i)^2$
CENAM	99.642 0	0.001 3	58959745	591715.976	0.929
IPQ	99.643 8	0.000 77	168061722	1686625.06	0.553
VSL	99.643 9	0.001 9	27602178.6	277008.31	0.114
SP	99.644 7	0.001 5	44286511.1	444444.444	0.906
INRIM	99.643 6	0.000 83	144641605	1451589.49	0.209
NIM	99.639 1	0.001 4	50836278.4	510204.082	8.645
INMETRO	99.643 3	0.000 48	432479774	4340277.78	0.060
		Σ	926867815	9301865.14	11.418
			x_{ref}/mL	99.643 22	$\chi^2_{0.05,6}$ = 12.6
			$u(x_{\mathrm{ref}})$/mL	0.000 33	pass

Figure 3. Measurement results for TS 03.01.12. Horizontal solid bold line represents the KCRV, calculated according to Cox method. Uncertainties are expressed at k = 2.

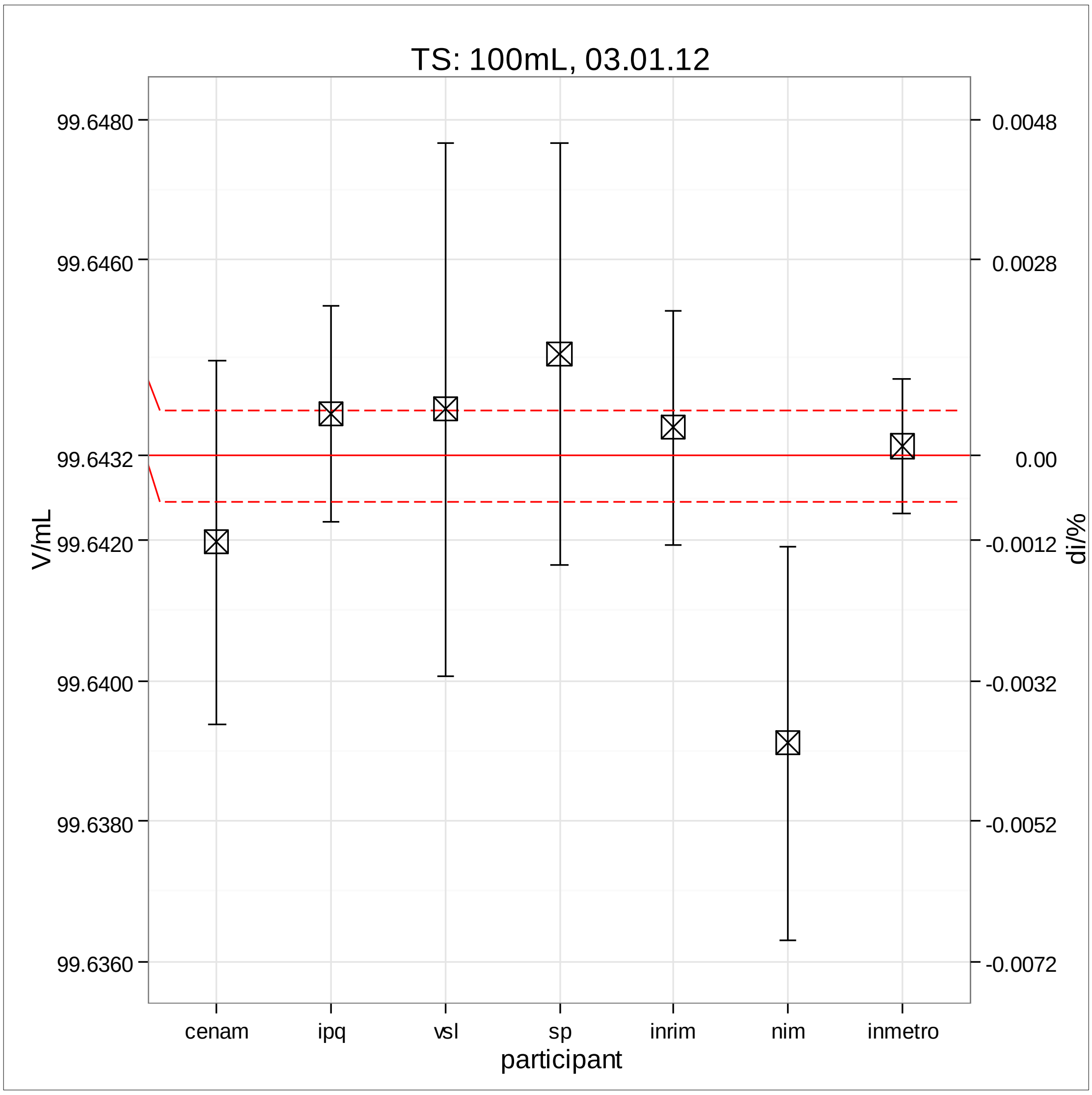


Table 12. Consistency check and computation of KCRV for TS 03.01.16.

TS 03.01.16	x_i/mL	$u(x_i)$/mL	$x_i/u(x_i)^2$	$1/u(x_i)^2$	$(x_i - x_{ref})^2/u(x_i)^2$
CENAM	103.090 8	0.001 3	61000480.5	591715.976	0.711
IPQ	103.092 0	0.000 80	161081205	1562500	0.006
VSL	103.091 9	0.001 9	28557299.6	277008.31	0.001
SP	103.094 0	0.001 5	45819555.6	444444.444	1.945
INRIM	103.092 1	0.000 83	149647431	1451589.49	0.062
NIM	103.091 1	0.001 1	85199265.9	826446.281	0.524
INMETRO	103.091 9	0.000 46	487201828	4725897.92	0.000
		Σ	1018507065	9879602.42	3.249
			x_{ref}/mL	103.091 91	$\chi^2_{0.05,6}$ = 12.6
			$u(x_{ref})$/mL	0.000 32	pass

Figure 4. Measurement results for TS 03.01.16. Horizontal solid bold line represents the KCRV, calculated according to Cox method. Uncertainties are expressed at k = 2.

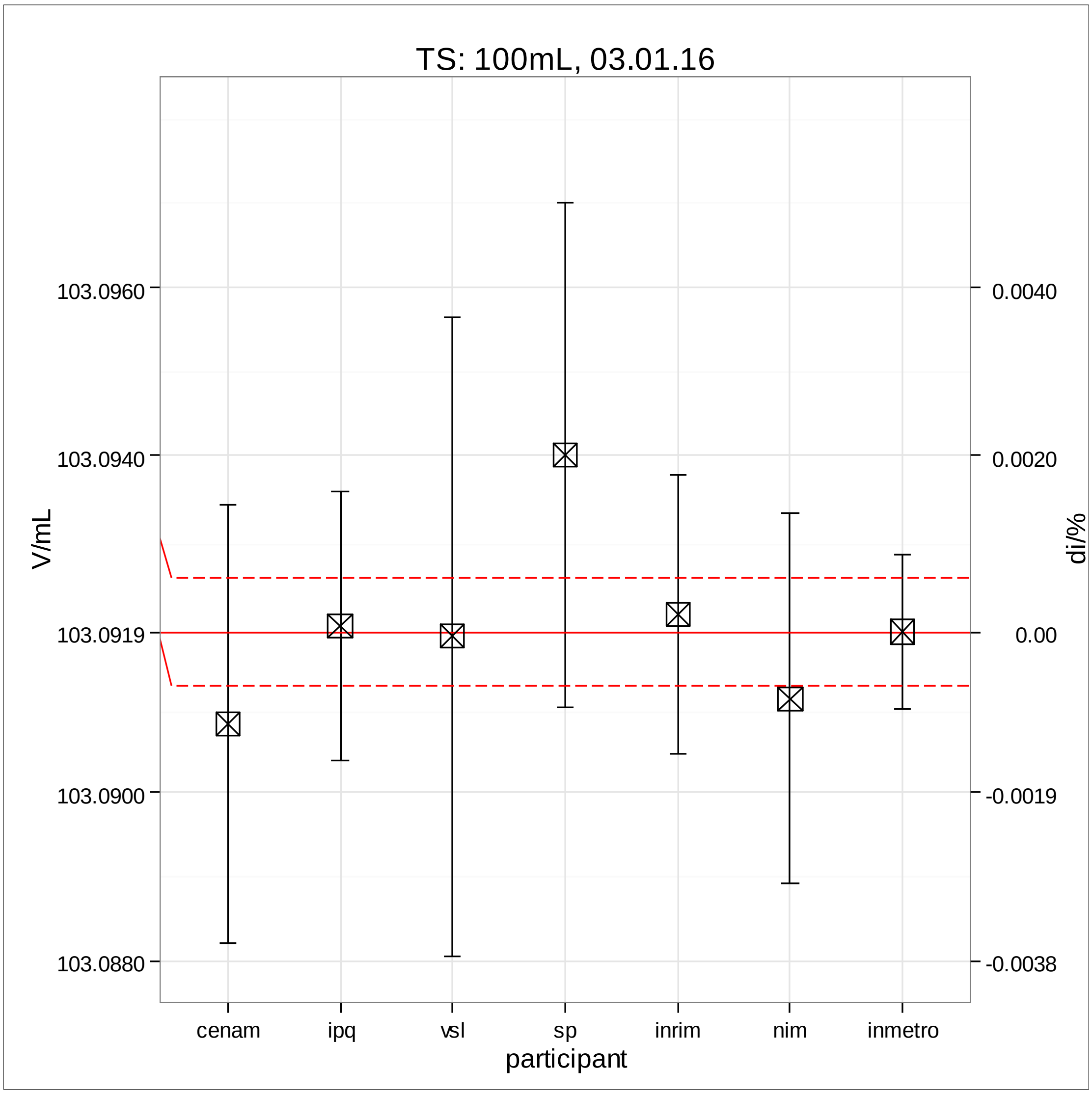
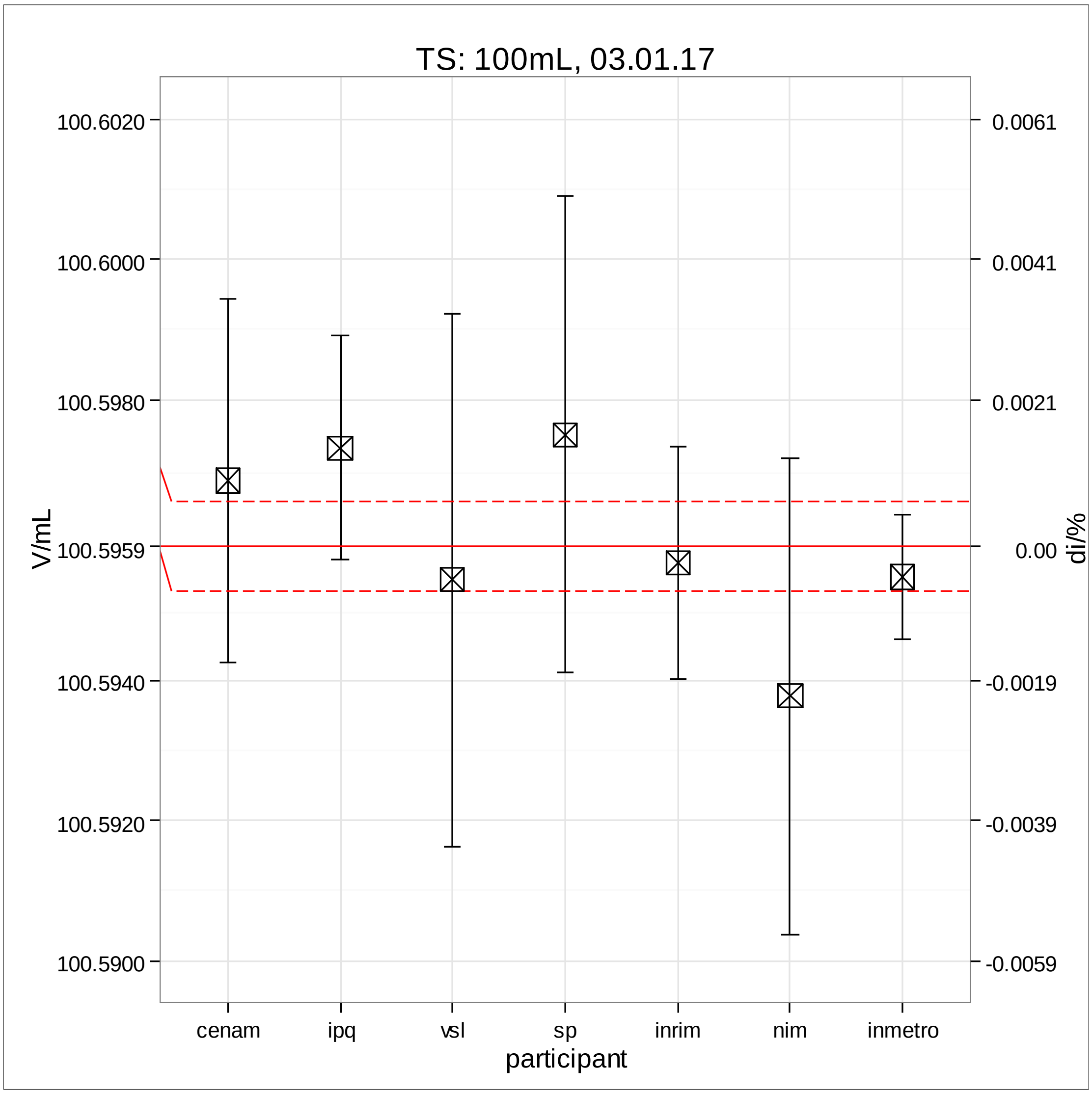


Table 13. Consistency check and computation of KCRV for TS 03.01.17.

TS 03.01.17	x_i/mL	$u(x_i)$/mL	$x_i/u(x_i)^2$	$1/u(x_i)^2$	$(x_i - x_{ref})^2/u(x_i)^2$
CENAM	100.596 8	0.001 3	59524759.2	591715.976	0.538
IPQ	100.597 3	0.000 80	157183295	1562500	3.149
VSL	100.595 4	0.001 9	27865770.1	277008.31	0.058
SP	100.597 5	0.001 7	34808823.5	346020.761	0.898
INRIM	100.595 7	0.000 83	146023625	1451589.49	0.067
NIM	100.593 8	0.001 7	34807531.9	346020.761	1.558
INMETRO	100.595 5	0.000 44	519604700	5165289.26	0.909
		Σ	979818505	9740144.56	7.177
			x_{ref}/mL	100.595 89	$\chi^2_{0.05,6}$ = 12.6
			$u(x_{ref})$/mL	0.000 32	pass

Figure 5. Measurement results for TS 03.01.17. Horizontal solid bold line represents the KCRV, calculated according to Cox method. Uncertainties are expressed at k = 2.



9. DETERMINATION OF THE DEGREES OF EQUIVALENCE (DoE)

9.1 Volume at 20 L

Tables 14, 15. Degree of equivalence for Volume of Liquids at 20 L

TS 710–04					CENAM		NIST		IPQ		VSL		SP		INRIM		NIM		INMETRO	
NMI	$\frac{d_i}{x_{ref}}\cdot 10^6$	$\frac{U(d_i)}{x_{ref}}\cdot 10^6$	$E_n(x_i)$		$\frac{d_{ij}}{\bar{x}_{ij}}\cdot 10^6$								$\frac{U(d_{ij})}{\bar{x}_{ij}}\cdot 10^6$							
CENAM	–0.08	39	–0.002				–8.7	70	2.7	94	11	53	6.4	47	1.0	44	15	50	–15	45
NIST	8.6	57	0.15		8.7	70			11	103	19	67	15	63	9.6	61	24	65	–6.3	61
IPQ	–2.7	84	–0.03		–2.7	94	–11	103			8.1	92	3.7	89	–1.7	87	12	90	–18	87
VSL	–11	32	–0.33		–11	53	–19	67	–8.1	92			–4.4	42	–9.8	39	4.1	45	–26	39
SP	–6.5	23	–0.28		–6.4	47	–15	63	–3.7	89	4.4	42			–5.4	31	8.5	39	–21	32
INRIM	–1.05	16	–0.06		–1.0	44	–9.6	61	1.7	87	9.8	39	5.4	31			14	36	–16	28
NIM	–15	28	–0.53		–15	50	–24	65	–12	90	–4.1	45	–8.5	39	–14	36			–30	36
INMETRO	15	17	0.86		15	45	6.3	61	18	87	26	39	21	32	16	28	30	36		

TS 710–05					CENAM		NIST		IPQ		VSL		SP		INRIM		NIM		INMETRO	
NMI	$\frac{d_i}{x_{ref}}\cdot 10^6$	$\frac{U(d_i)}{x_{ref}}\cdot 10^6$	$E_n(x_i)$		$\frac{d_{ij}}{\bar{x}_{ij}}\cdot 10^6$								$\frac{U(d_{ij})}{\bar{x}_{ij}}\cdot 10^6$							
CENAM	–1.4	39	–0.04				5.9	70	27	80	13	53	2.8	47	–2.3	44	18	50	–15	43
NIST	–7.3	57	–0.13		–5.9	70			21	90	7.0	67	–3.1	63	–8.2	61	12	65	–21	60
IPQ	–28	68	–0.41		–27	80	–21	90			–14	77	–24	73	–29	72	–8.8	75	–42	71
VSL	–14	33	–0.44		–13	53	–7.0	67	14	77			–10	42	–15	39	5.1	45	–28	38
SP	–4.2	23	–0.18		–2.8	47	3.1	63	24	73	10	42			–5.1	31	15	39	–18	30
INRIM	0.9	16	0.05		2.3	44	8.2	61	29	72	15	39	5.1	31			20	36	–13	26
NIM	–19	28	–0.68		–18	50	–12	65	8.8	75	–5.1	45	–15	39	–20	36			–33	34
INMETRO	14	14	0.97		15	43	21	60	42	71	28	38	18	30	13	26	33	34		

9.2 Volume of liquids at 100 mL

Tables 16, 17. Degree of equivalence for Volume of Liquids at 100 mL

TS 03.01.12					CENAM		IPQ		VSL		SP		INRIM		NIM		INMETRO	
NMI	$\frac{d_i}{x_{\text{ref}}}\cdot 10^6$	$\frac{U(d_i)}{x_{\text{ref}}}\cdot 10^6$	$E_n(x_i)$		$\frac{d_{ij}}{\bar{x}_{ij}}\cdot 10^6$								$\frac{U(d_{ij})}{\bar{x}_{ij}}\cdot 10^6$					
CENAM	–13	25	–0.50				–18	30	–19	46	–27	40	–16	31	29	38	–14	28
IPQ	5.7	14	0.41		18	30			–0.7	41	–8.6	34	1.9	23	47	32	4.6	18
VSL	6.4	38	0.17		19	46	0.7	41			–7.9	49	2.6	42	48	47	5.3	39
SP	14	29	0.49		27	40	8.6	34	7.9	49			11	34	56	41	13	32
INRIM	3.8	15	0.25		16	31	–1.9	23	–2.6	42	–11	34			45	33	2.6	19
NIM	–41	27	–1.51		–29	38	–47	32	–48	47	–56	41	–45	33			–42	30
INMETRO	1.2	7.0	0.17		14	28	–4.6	18	–5.3	39	–13	32	–2.6	19	42	30		

TS 03.01.16					CENAM		IPQ		VSL		SP		INRIM		NIM		INMETRO	
NMI	$\frac{d_i}{x_{\text{ref}}}\cdot 10^6$	$\frac{U(d_i)}{x_{\text{ref}}}\cdot 10^6$	$E_n(x_i)$		$\frac{d_{ij}}{\bar{x}_{ij}}\cdot 10^6$								$\frac{U(d_{ij})}{\bar{x}_{ij}}\cdot 10^6$					
CENAM	–11	24	–0.45				–11	30	–10	45	–31	39	–13	30	–2.9	33	–11	27
IPQ	0.63	14	0.04		11	30			1.2	40	–20	33	–1.4	22	8.3	26	0.6	18
VSL	–0.57	36	–0.02		10	45	–1.2	40			–21	47	–2.6	40	7.2	43	–0.5	38
SP	21	28	0.74		31	39	20	33	21	47			18	33	28	36	20	30
INRIM	2.1	15	0.14		13	30	1.4	22	2.6	40	–18	33			10	27	2.0	18
NIM	–8.0	20	–0.39		2.9	33	–8.3	26	–7.2	43	–28	36	–10	27			–7.7	23
INMETRO	–0.01	6.4	0.00		11	27	–0.6	18	0.5	38	–20	30	–2.0	18	7.7	23		

Table 18. Degree of equivalence for Volume of Liquids at 100 mL (artifact 03.01.17)

TS 03.01.17	$\frac{d_i}{x_{\mathrm{ref}}} \cdot 10^6$	$\frac{U(d_i)}{x_{\mathrm{ref}}} \cdot 10^6$	$E_{\mathrm{n}}(x_{\mathrm{i}})$		CENAM		IPQ		VSL		SP		INRIM		NIM		INMETRO	
NMI					$\frac{d_{ij}}{\bar{x}_{ij}} \cdot 10^6$	$\frac{U(d_{ij})}{\bar{x}_{ij}} \cdot 10^6$	$\frac{d_{ij}}{\bar{x}_{ij}} \cdot 10^6$	$\frac{U(d_{ij})}{\bar{x}_{ij}} \cdot 10^6$	$\frac{d_{ij}}{\bar{x}_{ij}} \cdot 10^6$	$\frac{U(d_{ij})}{\bar{x}_{ij}} \cdot 10^6$	$\frac{d_{ij}}{\bar{x}_{ij}} \cdot 10^6$	$\frac{U(d_{ij})}{\bar{x}_{ij}} \cdot 10^6$	$\frac{d_{ij}}{\bar{x}_{ij}} \cdot 10^6$	$\frac{U(d_{ij})}{\bar{x}_{ij}} \cdot 10^6$	$\frac{d_{ij}}{\bar{x}_{ij}} \cdot 10^6$	$\frac{U(d_{ij})}{\bar{x}_{ij}} \cdot 10^6$	$\frac{d_{ij}}{\bar{x}_{ij}} \cdot 10^6$	$\frac{U(d_{ij})}{\bar{x}_{ij}} \cdot 10^6$
CENAM	10	25	0.38				–4.6	30	14	46	–6.5	43	12	31	31	43	14	27
IPQ	14	15	0.98		4.6	30			19	41	–1.9	37	16	23	35	37	18	18
VSL	–4.6	37	–0.12		–14	46	–19	41			–21	51	–2.4	41	17	51	0	39
SP	16	33	0.49		6.5	43	1.9	37	21	51			18	38	37	48	20	35
INRIM	–2.2	15	–0.14		–12	31	–16	23	2.4	41	–18	38			19	38	2.0	19
NIM	–21	33	–0.64		–31	43	–35	37	–17	51	–37	48	–19	38			–17	35
INMETRO	–4.2	6	–0.70		–14	27	–18	18	0	39	–20	35	–2.0	19	17	35		

10. CMC CONSISTENCY CHECK

In order to judge on the support that this comparison results support CMC entries, it is necessary to compare d_i against declared uncertainty values from the CMC tables. It is expected that d_i values are smaller than U_{CMCs} for supporting purposes.

Table 19. Consistency check for CMC entries for volume of liquids at 20 L.

NMI	U_{CMCs}	$U_{\mathrm{K4.1.2011}}$	$\frac{d_i}{x_{\mathrm{ref}}}$	Are the CMCs supported by CCM.FF-K4.1.2011
	%	%	%	
CENAM	0.004 0	0.004 0	0.000 016	yes
NIST	0.015 + 1.2/V, V in L	0.005 8	0.000 15	yes
IPQ	0.01	0.008 5	–0.001 5	yes
VSL	0.01	0.003 4	–0.001 2	yes
SP	0.003	0.002 5	–0.000 44	yes
INRIM	0.005	0.001 9	0.000 082	yes
NIM	n/a	0.003 0	–0.001 6	n/a
INMETRO	0.010	0.002 0	0.001 5	yes

Table 20. Consistency check for CMC entries for volume of liquids at 100 mL.

NMI	U_{CMCs}	$U_{\mathrm{K4.1.2011}}$	$\frac{d_i}{x_{\mathrm{ref}}}$	Are the CMCs supported by CCM.FF-K4.1.2011
	%	%	%	
CENAM	0.004	0.0026	–0.0005	yes
IPQ	0.003	0.0016	0.0007	yes
VSL	0.01	0.0038	0.0000	yes
SP	0.003	0.0031	0.0017	yes
INRIM	0.005	0.0016	0.0001	yes
NIM	n/a	0.0028	–0.0024	n/a
INMETRO	0.004	0.0009	–0.0001	yes

11. CONCLUSIONS

i. CCM.FF-K4.1.2011 for Volume of Liquids at 20 L and 100 mL was conducted during 2012 – 2014. The execution of the CCM.FF-K4.1.2011 was affected by the fact that the transfer package remained at the Brazilian Customs for nearly 8 months; despite this fact, the artifacts did not change their metrological properties, and the KC was completed successfully.

ii. CCM.FF-K4.1.2011 was piloted by CENAM. Eight NMIs tested the two 20 L transfer standards, whereas 7 tested the three 100 mL pycnometers.

iii. No discrepant measurements were distinguished on the 20 L artifacts. The largest difference between two NMIs was 0.004 2 %; whereas the average degree of equivalence $\bar{d}_{i,j}$, for artifacts 710-04 and 710-05 resulted in 0.000 1 % and 0.000 5 %, respectively.

iv. Only one participant produced anomalous results for 100 mL measurements; NIM´s result for TS 03.01.12 was inconsistent with IPQ, VSL, SP, INRIM and INMETRO. However, results for artifacts 03.01.16 and 03.01.17 were all fully consistent with each other. The average degree of equivalence $\bar{d}_{i,j}$, for artifacts 03.01.16 and 03.01.17 resulted in 0.000 17 % and 0.001 1 %, respectively.

v. Subsequent linkage to CCM.FF-K4.1.2011 will be based on the results for artifacts 710-04 and 03.01.17, for 20 L and 100 mL, respectively.

12. REFERENCES

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13. FIGURES

Figure 6. Photograph of the assembled 20 L transfer standard.

Figure 7. An image of the Gay-Lussac type pycnometers for volumes of 100 mL.

Appendix A
UNCERTAINTY CONTRIBUTIONS

Table A1. Uncertainty contributions (in milliliters) to the uncertainty of the measurand at 20 L.

<table>
<tr><th>20 L
- contributions in mL -</th><th>CENAM</th><th>NIST</th><th>IPQ</th><th>VSL</th><th>SP</th><th>INRIM</th><th>NIM</th><th>INMETRO</th></tr>
<tr><td>Balance</td><td>0.17</td><td></td><td>0.21</td><td>0.020</td><td>0.004 6</td><td>0.058</td><td>0.032</td><td></td></tr>
<tr><td>Weights</td><td>0.012</td><td>0.22</td><td>0.031</td><td>0.022</td><td>0.056</td><td>0.011</td><td>0.028</td><td>0.022</td></tr>
<tr><td>water temperature (calibration)</td><td rowspan="2">0.33</td><td rowspan="2">0.13</td><td>0.014</td><td>0.20</td><td>0.000</td><td>0.060</td><td>0.072</td><td rowspan="2">0.0043</td></tr>
<tr><td>Temperature gradients</td><td></td><td rowspan="2">0.24</td><td>0.000</td><td>0.046</td><td>0.28</td></tr>
<tr><td>water density</td><td>0.008</td><td>0.2</td><td>0.026</td><td>0.23</td><td>0.10</td><td>0.062</td><td>0.12</td></tr>
<tr><td>air temperature</td><td>0.005</td><td rowspan="3">0.04</td><td></td><td>0.006 8</td><td>0.000</td><td>0.016</td><td>0.023</td><td>0.000</td></tr>
<tr><td>Ambient pressure</td><td>0.003</td><td></td><td>0.01</td><td>0.000</td><td>0.005</td><td>0.008</td><td>0.001</td></tr>
<tr><td>Relative humidity</td><td>0.001</td><td></td><td>0.002 4</td><td>0.000</td><td>0.004</td><td>0.004</td><td>0.000</td></tr>
<tr><td>Artifact temperature</td><td></td><td></td><td></td><td></td><td>0.000</td><td>0.095</td><td></td><td></td></tr>
<tr><td>Thermal expansion coefficient</td><td>0.078</td><td>0.01</td><td>0.068</td><td>0.06</td><td>0.000</td><td>0.004</td><td>0.034</td><td>0.002</td></tr>
<tr><td>Leaks</td><td rowspan="3">0.12</td><td></td><td></td><td></td><td>0.0081</td><td></td><td></td><td></td></tr>
<tr><td>Evaporation</td><td></td><td>0.29</td><td></td><td>0.058</td><td></td><td></td><td></td></tr>
<tr><td>Clingage</td><td></td><td>0.58</td><td></td><td>0.027</td><td>0.058</td><td></td><td></td></tr>
<tr><td>Repeatability</td><td>0.023</td><td>0.47</td><td>0.082</td><td>0.018</td><td>0.015</td><td>0.040</td><td>0.03</td><td>0.079</td></tr>
<tr><td>Others</td><td></td><td></td><td></td><td>0.10</td><td>0.059</td><td></td><td></td><td>0.077</td></tr>
<tr><td>combined uncertainty; $u(V_{20})$/mL</td><td>0.40</td><td>0.58</td><td>0.69</td><td>0.34</td><td>0.25</td><td>0.19</td><td>0.30</td><td>0.17</td></tr>
<tr><td>expanded uncertainty; $U(V_{20})$/mL</td><td>0.80</td><td>1.2</td><td>1.4</td><td>0.68</td><td>0.52</td><td>0.38</td><td>0.65</td><td>0.34</td></tr>
</table>

Table A2. Uncertainty contributions (in milliliters) to the uncertainty of the measurand at 100 mL.

100 mL - contributions in µL -	CENAM	IPQ	VSL	SP	INRIM	NIM	INMETRO
Balance	0.21	0.041	0.22	0.018	0.030	0.047	0.017
Weights	0.11	0.048	0.11	0.19	0.11	0.14	0.12
water temperature (calibration)	1.2		1.21	0.056	0.51	0.055	0.005
Temperature gradients				0.61	0.20	0.050	
water density		0.13	0.65	1.1	0.50	0.29	0.23
air temperature	0.14	0.026	0.035	0.004	0.087	0.075	0.31
Ambient pressure			0.049	0.10	0.022	0.052	0.12
Relative humidity			0.012	0.005	0.024	0.036	0.079
Artifact temperature	0.00			0.029	0.10		
Thermal expansion coefficient	0.00	0.051	0.17	0.04	0.031	0.013	0.000
Leaks							
Evaporation					0.30		
Clingage							
Repeatability	0.13	0.78	0.18	0.60	0.11	1.3	0.26
Others			1.2	0.48			
combined uncertainty; $u(V_{20})$/mL	1.3	0.80	1.9	1.47	0.83	1.35	0.48
expanded uncertainty; $U(V_{20})$/mL	2.6	1.6	3.8	3.0	1.7	2.64	0.98

Appendix B
EQUIPMENT DESCRIPTION AND TRACEABILITY STATEMENTS

Table B1. Traceability information for measurements at 20 L. Values in red correspond to standard uncertainty.

20 L	BALANCE	WEIGHTS	THERMOMETER	PRESSURE	HUMIDITY METER	TRACEABILITY
CENAM	Mettler XP64002L 64 kg/0.01 g/0.050 g	Rice Lake E2 + Masstech F1	Vaisala HM34 $u(t)$ = 0.2 °C	Druck DPI 740 $u(p)$ = 4.5 Pa	Vaisala HM34 $u(hr)$ = (0.25 – 0.55) %	CENAM
NIST	Mettler KB50-2/49 60 kg/0.1 g/0.2 g	Rice Lake 5 ppm	Thermister Fluke Chub E4 0.3 °C	Vaisala PTU 200 0.15%	Vaisala PTU 200 2.5%	NIST
IPQ	MettlerKCC100 150 kg/0.05 g/0.039 g	SartoriousF1 0.017 g	Hygroclip 0.05 °C	Druck DPI 142 15 Pa	Hygroclip 0.05 %	IPQ
VSL	Sartorious CCE60K2 64 kg/0.01 g/	OIML class E2	Novasina HygroDat 100 0.05 °C	Druck DPI 142 18 Pa	Novasina HygroDat 100 0.35 %	VSL
SP	Mettler KA30-3 30 kg/0.005 g/		Testoterm 610 0.1 °C	Paulin Linod 20 Pa	Testoterm 610 0.1 %	
INRIM	Mettler PK60 60 kg/0.01 g/	OIML F1	MBW 473 0.02 °C	Ruska PPG 220 3 Pa	MBW 473 0.2 %	INRIM
NIM	Mettler XP26003L 26 kg/0.001 g/0.01 g	OIML E2	HART 1521 0.01 °C	China CST2008 10 Pa	Vaisala HM34C	NIM
INMETRO	Sartorious C 60000S 60 kg/0.01 g/0.025 g	Haefner E2	Oregon Sc. BAR988 0.15 °C	Oregon Sc. BAR988 60 Pa	Oregon Sc. BAR988 0.8 %	INMETRO

Table B2. Traceability information for measurements at 100 mL. Values in red correspond to standard uncertainty.

100 mL	BALANCE	WEIGHTS	THERMOMETER -air temperature-	PRESSURE	HUMIDITY METER	THERMOMETER -water temp-	TRACEABILITY
CENAM	Mettler XP205 220 g/0.01 mg/0.17 mg	Rice Lake E2	Vaisala HM34C 0.2 °C	Barometer Druck DPI 740 4 Pa	Vaisala HM34C 0.9 %	ERTCO 0.03 °C	CENAM
IPQ	Mettler XP205 220 g/0.01 mg/0.06 mg	Mettler OIML E2	Hygroclip 0.05 °C	Druck DPI 142 15 Pa	Hygroclip 0.05 %	Luft C100 0.01 °C	IPQ
VSL	Mettler AG245 210g/0.1 mg/	OIML E2	Novasina HygroDat 100 0.05 °C	Druck DPI 142 18 Pa	Novasina HygroDat 100 0.35 %	Beamex MC5-IS 0.01 °C	VSL
SP	Mettler AT-201 200 g/0.01 mg/	Mettler	Testoterm Testo 610 0.1 °C	Paulin, Linod 20Pa	Testoterm Testo 610 0.1 %	ASL F250 0.001 °C	SP
INRIM	Mettler AT 400 400 g/0.01 mg/	OIML E2	MBW 473 0.02 °C	Ruska PPG 6200 3 Pa	MBW 473 0.2 %	ASL F700 + Pt-100 0.015 °C	INRIM
NIM	Mettler XP205 220 g/0.01 mg/0.058 mg	OIML E2	Vaisala HM34C 0.2 °C	Barigo 50 Pa	Vaisala HM34C 4 %	JW-1 0.01 °C	NIM
INMETRO	Sartorious ME215S 210 g/0.01 mg/0.07 mg	Haefner OIML E2	Oregon Sc. BAR988 0.15 °C	Oregon Sc. BAR988 80 Pa	Oregon Sc. BAR988 0.7 %	Anton Paar MKT 50 0.005 °C	INMETRO

Appendix C

Kenya Bureau of Standards (KEBS) results

	03.01.12	**03.01.16**	**03.01.17**	**710-04**	**710-05**
1	100.38537	101.05249	100.23903	19996.62766	20011.47569
2	100.39885	101.11071	99.55153	19996.40645	20000.23041
3	100.42171	101.07388	100.16947	19995.27158	20008.09756
4	100.40384	100.00221	100.07144	19996.96259	20001.69259
5	100.40594	100.99227	100.07753	19911.14928	20007.06145
6	100.39480	101.05910	100.07219	20007.25018	20011.12902
7	100.39770	101.01933	100.12978	19941.84351	20006.06801
8	100.41627	101.06263	99.99408	19995.84273	20010.09272
9	100.40768	101.09638	99.99089	19959.56563	20010.21790
10	100.43811	101.08232	99.87730	19980.42162	20010.32701
mean	100.40703	100.95513	100.01732	19978.13412	20007.63924
sd	0.01510	0.33662	0.19216	30.98285	3.94484