Final Report
on

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

Conducted May 2018 to November 2024

SIM.M.FF-K4.1.2017

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CONTENT

1. INTRODUCTION

At its meeting in April 2015 in Washington D.C., the Inter-American Metrology System (SIM) Technical Committee for Fluid Flow (SIM MWG10) 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 of liquids comparison is identified as SIM.M.FF-K4.1.2017 and performed with the intention to compare the performance of the participating NMIs regarding the determination of the volume of liquids at 20 L and 100 mL.

Despite not being a SIM NMI or Designated Institute, and due to its high technical capabilities, Measurement Canada, MC, was invited to participate in this Regional Comparison. Its measurement results do not contribute to the Comparison Reference Value.

During the measurements, CENAMEP AIP decided to withdraw from the comparison.

2. SELECTED CONDITIONS

The participating laboratories determined the volume of water that the two 20 L Transfer Standards (TS) are able to **deliver** after a period of dripping-off time in accordance with the Technical Protocol, 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 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 are 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.

The 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 will compile and analyze the results according to the MRA rules, and after review by the participants, Draft B will be proposed for publication in the KCDB.

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. The comparison execution program suffered significant delays due to the Covid-19 pandemic and delays in customs clearance processes.

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

NMI		Date month/day, year	Contact	Remarks
CENAM	Mexico	May, 2018	Manuel Maldonado mmaldona@cenam.mx	Pilot, CCM.FF-K4.1.2011 link
MC*	Canada	July, 2018	Luigi Buffone Luigi.Buffone@Canada.ca	Invited
NIST	USA	August, 2018	John D. Wright, Sherry Sheckels john.wright@nist.gov sherry.scheckels@nist.gov	SIM participant, CCM.FF-K4.1.2011 link
LACOMET, RECOPE	Costa Rica	December, 2018	Luis D. Rodríguez lrodriguez@lacomet.go.cr Jorge Delgado jorge.delgado@recope.go.cr	SIM participant
CENAMEP AIP**	Panama	February, 2019	Orlando Pinzón opinzon@cenamep.org.pa	SIM participant
INM	Colombia	June, 2019	Stivinson Córdoba scordoba@inm.gov.co	SIM participant
INACAL	Peru	May, 2020	Abed Morales amorales@inacal.gob.pe	SIM participant
IBMETRO	Bolivia	March, 2021	Juan José Mendoza jjmendoza@ibmetro.gob.bo	SIM participant
INTN	Paraguay	August, 2021	Diana Cantero dcantero@intn.gov.py	SIM participant
INMETRO	Brazil	September, 2021	Jose M. Gouveia jmgouveia@inmetro.gov.br	SIM participant, CCM.FF-K4.1.2011 link
LATU	Uruguay	October, 2023	Andrea Sica asica@latu.org.uy	SIM Participant
INTI	Argentina	April, 2024	Rubén Quille rquille@inti.gob.ar Carlos Comi ccomi@inti.gob.ar Laura de la Asunción lasuncion@inti.gob.ar	SIM Participant
CENAM	Mexico	November, 2024	Manuel Maldonado	

*Measurement Canada (MC) is not a Designated Institute; however, due to its high proficiency in the field of Volume of Liquids was invited to take part of this comparison exercise. According to the MRA rules, its measurement results will not be taken into account for the calculation of the Comparison Reference Value (*CRV*). Its results and how these compares to other NMIs are included in Annex A.

**CENAMEP AIP received and tested the TSs; however, due to internal issues, decided to withdraw from the comparison.

4. THE TRANSFER PACKAGES

4.1 **Transfer Package for** 20 L

4.1.1 Overflow type pipette

The TS consisted of: a) the 20 L pipette, b) a hand held digital thermometer, c) fittings for assembling and disassembling.

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.

Fig. 1. Image of the overflow type 20 L pipette. TS 710-05.

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 20 N·m for assembling purposes.

4.1.2 Graduated neck test measure

This transfer standard is a 20 L commercially available volumetric test measure, equipped with graduated neck reading scale, with resolution of 5 mL. This artifact was calibrated by the participants to determine the quantity of delivered water, at a reference temperature of 20 °C.

Fig. 2. Image of the 20 L graduated neck test measure.
TS 04.

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. 3). 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 3.3×10^{-6} °C^{-1}; this value is transformed to a cubic expansion coefficient of $(9.9 \pm 1) \times 10^{-06}$ °C^{-1}.

Fig. 3. Image of the TS for 100 mL. Glass pycnometers 03.01.15 and 03.01.17.

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.

<table>
<tr><td colspan="2" rowspan="2"></td><td colspan="6">Day of test</td></tr>
<tr><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td></tr>
<tr><td rowspan="5">Measurements per day</td><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_1</td><td></td><td rowspan="5">Packaging of the TSs for shipment to next NMI.</td></tr>
<tr><td>2</td><td>x_2</td><td>x_2</td><td></td></tr>
<tr><td>3</td><td>x_3</td><td>x_3</td><td></td></tr>
<tr><td>4</td><td>x_4</td><td>x_4</td><td></td></tr>
<tr><td>5</td><td>x_5</td><td>x_5</td><td></td></tr>
</table>

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

6. EXPERIMENTAL PROCEDURE

All participating NMIs applied 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

NMI	Weighing*		Water**	Deaerated water?	Density formula
	20 L	100 mL			
CENAM	DS	DR	IE + O	No	Tanaka [1]
MC	DR		B	No	Tanaka
NIST	SS		O	No	Patterson & Morris [2]
LACOMET, RECOPE	SS	SS	O + F + Di	No	Tanaka
INM	DR	DR	O	Yes	Tanaka
INACAL	DR	DR	1D	No	Tanaka
IBMETRO	DR	DR	1D	No	Tanaka
INTN	DR	DR	1D	No	Tanaka
INMETRO	DR	DR	F	No	Measured
LATU	DR	DR	1D	No	Tanaka
INTI	DS	DR	O + Di	No	Tanaka

Weighing: DS: Double substitution; DR: direct reading; SS: single substitution.
****water:*** B: Boiled; IE: Ion exchange; F: Filtered; O: Reverse osmosis; 1D: single distillation; 2D: double distillation; Di: Deionized

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	CENAM	NIST	RECOPE	INM	INACAL	IBMETRO	INTN	INMETRO	LATU	INTI
	°C									
$\lvert t_d - 20 \rvert$	0.02	7.4	0.21	0.68	0.13	0.85	1.2	0.016	0.27	0.80
$\lvert t_w - t_a \rvert$	0.18	2.06	0.44	0.85	0.26	1.4	0.20	0.21	0.53	0.40

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 linking calculations to *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**	$\|\Delta V\|$
		$(x \pm u)$/mL		$(x \pm u)$/mL	mL
TS 710-05	05/2018	19 990.83 ± 0.38	12/2024	19 990.74 ± 0.38	0.09
TS 04	05/2018	20 004.30 ± 1.9	12/2024	20 004.9 ± 1.9	0.6

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

100 mL	date	**initial**	date	**final**	$\|\Delta V\|$
		$(x \pm u)$/mL		$(x \pm u)$/mL	mL
03.01.15	05/2018	97.811 3 ± 0.001 5	01/2025	97.809 6 ± 0.001 5	0.001 7
03.01.17	05/2018	100.982 6 ± 0.001 4	01/2025	100.980 6 ± 0.001 4	0.002 0

No substantial drift was observed either on the 20 L TS 710-05 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 *CRVs*.

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

TS 04, which definition of the volume is by meniscus reading at the graduated neck, has been tested by the pilot laboratory to determine the artifact uncertainty associated to the manipulation of the TS during the drainage operation. Different draining times (ranging from 20 s to 40 s) and different angles of TS´s draining position were evaluated. This uncertainty contribution u_{ts}, was characterized as having a uniform probability density function *pdf*, therefore, the numerical value of the standard uncertainty is calculated as:

$$u_{\text{ts}} = \frac{V_{\max} - V_{\min}}{\sqrt{12}} = \frac{3\text{ mL}}{\sqrt{12}} = 0.87\text{ mL} \quad (1)$$

This uncertainty will be propagated along with the uncertainty statements of each of the participants in order to calculate the *CRV* and degrees of equivalence, d_i.

Since 20 L pipette and the glass pycnometers were not prone to exhibit unstable behavior over time, nor affected by pouring operations, there will not be additional uncertainty components to be added to the original uncertainty statements for these artifacts.

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 and 04)

	20 L TS	TS 710-05 Overflow pipette		TS 04 Graduated neck	
#		x_i/mL	$u_{nmi}(x_i)$/mL	x_i/mL	$u_{nmi}(x_i)$/mL
1	CENAM	19 990.83	0.38	20 004.3	1.9
2	NIST	19 990.94	0.48	20 007.37	2.8
3	RECOPE	19 990.84	0.22	20 005.4	1.40
4	INM	19 989.39	0.35	20 005.18	1.5
5	INACAL	19 988.80	0.80	20 001.7	1.2
6	IBMETRO	19 989.16	0.96	20 005.84	1.7
7	INTN	19 990.28	1.57	20 006.02	1.01
8	INMETRO	19 991.20	1.46	20 007.38	0.95
9	LATU	19 990.80	1.03	20 008.4	1.53
10	INTI	19 990.70	0.41	20 004.8	0.76

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

	100 mL TSs	TS 03.01.15		TS 03.01.17	
#		x_i/mL	$u_{nmi}(x_i)$/mL	x_i/mL	$u_{nmi}(x_i)$/mL
1	CENAM	97.811 3	0.001 5	100.982 6	0.001 4
2	LACOMET	97.811 3	0.002 1	100.981 8	0.002 2
3	INM	97.812 5	0.000 59	100.983 3	0.000 57
4	INACAL	97.810 0	0.002 5	100.980 0	0.002 5
5	IBMETRO	97.818 8	0.001 7	100.985 9	0.001 5
6	INTN	97.811 3	0.002 0	100.981 5	0.002 9
7	INMETRO	97.810 2	0.000 76	100.980 2	0.000 75
8	LATU	97.813 5	0.002 1	100.984 4	0.002 2
9	INTI	97.811 3	0.001 9	100.981 5	0.002 4

7.3 Propagation of u_{ts} on the base uncertainty for the participants

Table 9 show the measurement results and the *"adjusted"* standard uncertainties, due to the propagation of u_{ts} along with the u_{base}, reported by the participants, according to the following expression:

$$u_{ad\_nmi} = \sqrt{u_{base}^2 + u_{ts}^2} \quad (2)$$

Table 9. Uncertainty adjusted values for the graduated neck 20 L TS 04.

	20 L TS	TS 04 Graduated neck	
#		x_i/mL	$u_{ad\_nmi}(x_i)$/mL
1	CENAM	20 004.3	2.09
2	NIST	20 007.37	2.93
3	RECOPE	20 005.4	1.65
4	INM	20 005.18	1.73
5	INACAL	20 001.7	1.48
6	IBMETRO	20 005.84	1.91
7	INTN	20 006.02	1.33
8	INMETRO	20 007.38	1.29
9	LATU	20 008.4	1.76
10	INTI	20 004.8	1.15

8. LINK TO CCM.FF-K4.1.2011 AND DEGREES OF EQUIVALENCE

8.1 TS 710-05, overflow type pipette

The degrees of equivalence were calculated by linking to the *KCRV* of the CCM key comparison CCM.FF−K4.1.2011, in which the TS 710-05 was used as one of the two 20 L pipettes supplied by CENAM.

The NMIs that are acting as linking NMIs are CENAM, NIST and INMETRO; however, due to the fact that the standard uncertainty that was reported by INMETRO for this SIM.M.FF-K4.1.2017 Key Comparison is 7 times larger than the standard uncertainty that INMETRO reported for CCM.FF-K4.1.2011; then, only the results from CENAM and NIST are considered as the linking values.

Table 10 lists the degrees of equivalence of the linking volume measurements on the TS No. 710-05 as determined in the CCM.FF-K4.1.2011 comparison. The *KCRV* value and the associated standard uncertainty of the TS710-05 were: $KCRV$ = 19 993.53 mL, $u(KCRV)$ = 0.096 mL.

Table 10. Degrees of equivalence for the linking laboratories in CCM.FF-K4.1.2011 comparison.

CCM.FF-K4.1.2011, TS 710-05		
	d_i/mL	$U(d_i)$/mL, $k = 2$
CENAM	−0.03	0.78
NIST	−0.14	1.14

The difference $d_{i\_\text{link\_CCM}}$, evaluated as weighted mean of the d_i of the linking laboratories was: $d_{i\_\text{link\_CCM}}$ = −0.065 mL, with a standard uncertainty $u(d_{i\_\text{link\_CCM}})$ = 0.32 mL; this result is used to correct the value obtained in this SIM comparison by the linking laboratories. In table 11, the results obtained by the linking laboratories in this comparison are given

Table 11. Results of the linking laboratories in SIM.M.FF-K4.1.2017.

SIM.M.FF-K4.1.2017, TS 710-05		
	x_i/mL	$u(x_i)$/mL
CENAM	19 990.83	0.38
NIST	19 990.94	0.48

From the results in table 11, by the weighted mean method the value $CRV_{\text{link\_SIM}}$ and the associated standard uncertainty $u(CRV_{\text{link\_SIM}})$ have been evaluated: $CRV_{\text{link\_SIM}}$ = 19 990.87 mL, and $u(CRV_{\text{link\_SIM}})$ = 0.30 mL.

In order to link the SIM.M.FF-K4.1.2017 comparison to the *KCRV* of the CCM.FF-K4.1.2011, the difference has been calculated as:

$$d_{\mathrm{CRV\_SIM-KCRV}} = CRV_{\mathrm{link\_SIM}} - d_{i\mathrm{\_link\_CCM}} - KCRV \quad (3)$$

$$d_{\mathrm{CRV\_SIM-KCRV}} = 19\,990.87\ \mathrm{mL} - (-0.065\ \mathrm{mL}) - 19\,993.53\ \mathrm{mL} = -2.595\ \mathrm{mL}$$

the standard uncertainty $u(d_{\mathrm{CRV\_SIM-KCRV}})$ can be computed by propagating the uncertainties due to $CRV_{\mathrm{link\_SIM}}$, $d_{i\mathrm{\_link\_CCM}}$ and *KCRV*, according to the following equation:

$$u(d_{\mathrm{CRV\_SIM-KCRV}}) = \sqrt{u(CRV_{\mathrm{link\_SIM}})^2 + u(di_{\mathrm{link\_CCM}})^2 + u(KCRV)^2} \quad (4)$$

$$u(d_{\mathrm{CRV\_SIM-KCRV}}) = \sqrt{(0.30)^2 + (0.32)^2 + (0.096)^2} = 0.45\ \mathrm{mL}$$

To calculate the degrees of equivalence d_i between the SIM laboratories results and the *KCRV*, the following formula is used

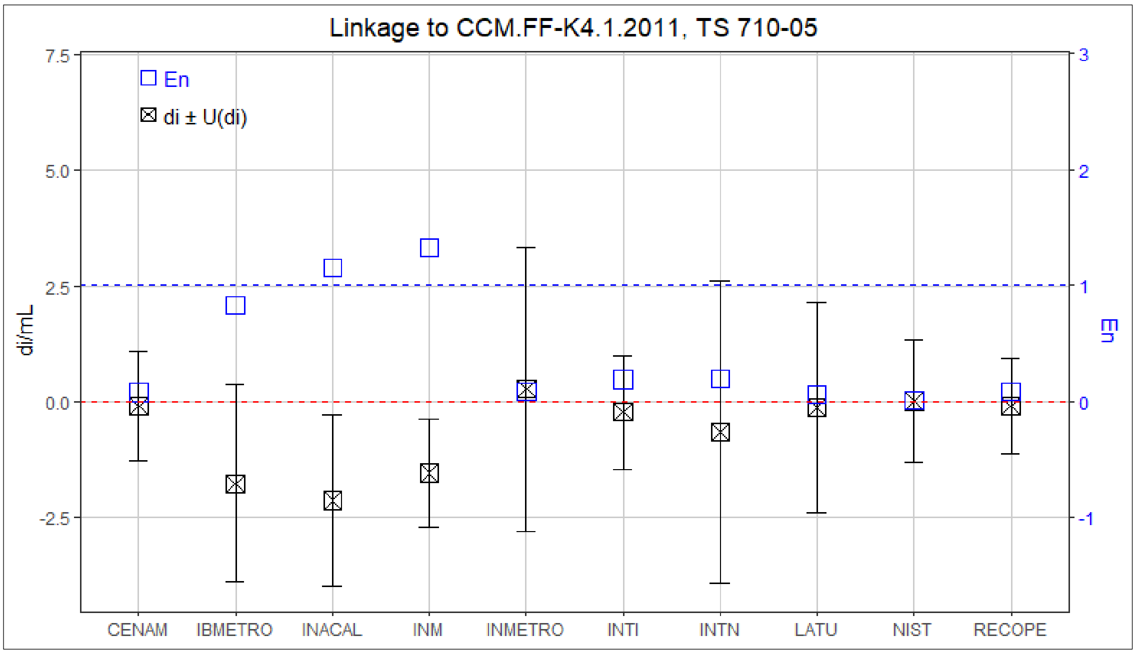
$$d_i = x_i - d_{\mathrm{CRV\_SIM-KCRV}} - KCRV \quad (5)$$

$$U(d_i) = 2\sqrt{u(x_i)^2 + u(d_{\mathrm{CRV\_SIM-KCRV}})^2 + u(KCRV)^2} \quad (6)$$

Table 12. Degrees of equivalence with *KCRV*, and the E_n value.

#	20 L TS	TS 710-05		
		d_i/mL	$U(d_i)$/mL	$\lvert E_{ni} \rvert$
1	CENAM	–0.10	1.19	0.08
2	NIST	0.01	1.33	0.01
3	RECOPE	–0.09	1.02	0.09
4	INM	–1.54	1.16	1.33
5	INACAL	–2.13	1.85	1.15
6	IBMETRO	–1.77	2.13	0.83
7	INTN	–0.65	3.27	0.20
8	INMETRO	0.27	3.06	0.09
9	LATU	–0.13	2.26	0.06
10	INTI	–0.23	1.23	0.19

Graph 1. Degrees of equivalence with *KCRV*, and the E_n value for TS 710-05; overflow type pipette for volume of liquids at 20 L.



8.2 20 L TS 04, graduated neck test measure

This type of artifact was not included in the CCM.FF-K4.1.2011; therefore, no linkage was calculated for this transfer standard.

The comparison reference value *CRV* for this artifact is calculated taking into account table 9 values. Cox methodology [4] was applied to compute the reference value. *CRV* resulted in (20 005.50 ± 0.50) mL, $k = 1$.

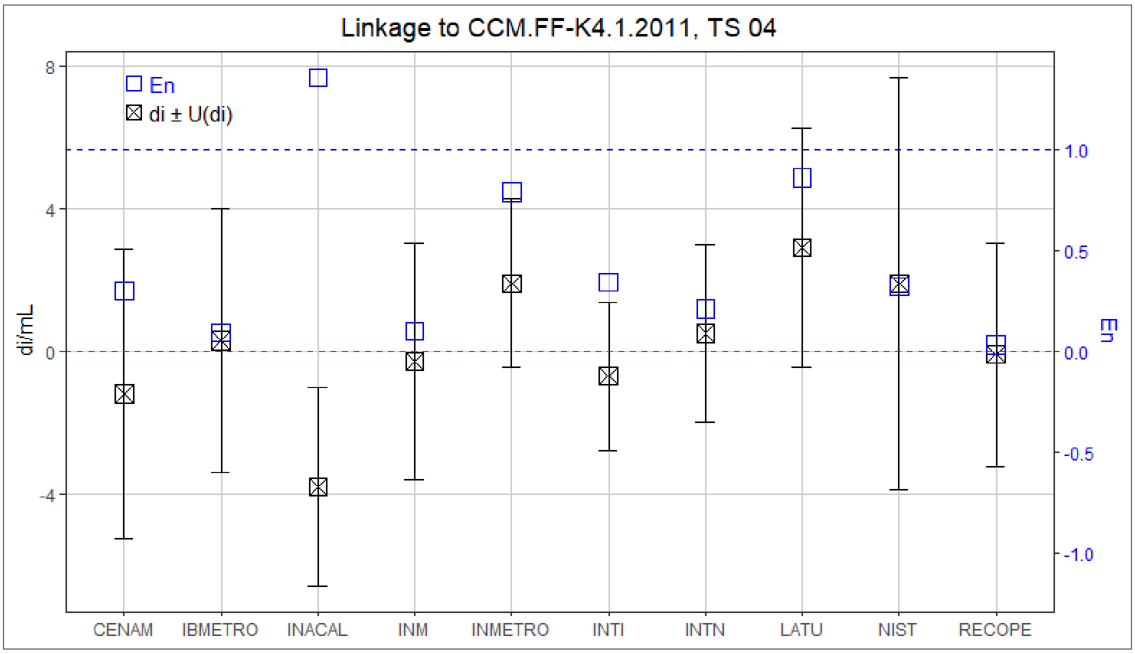
No results were found to fail the consistency check for this transfer standard artifact. Table 13 shows the degree of equivalence, d_i, expanded uncertainty, $U(d_i)$ and normalized error, E_n.

Table 13. Degrees of equivalence with *CRV*, and the E_n value for the TS-04, graduated neck test measure.

#	20 L TS	TS 04		
		d_i/mL	$U(d_i)$/mL**	$\lvert E_{ni} \rvert$
1	CENAM	−1.2	4.06	0.30
2	NIST	1.9	5.78	0.32
3	RECOPE	−0.1	3.14	0.03
4	INM	−0.3	3.32	0.10
5	INACAL	−3.8	2.79	1.36
6	IBMETRO	0.3	3.68	0.09
7	INTN	0.5	2.47	0.21
8	INMETRO	1.9	2.37	0.79
9	LATU	2.9	3.37	0.86
10	INTI	−0.7	2.08	0.34

** Expanded uncertainty, $U(d_i)$/mL is expressed with a coverage factor $k = 2$.

Graph 2. Degrees of equivalence with *CRV*, and the E_n value for TS 04; graduated neck test measure for volume of liquids at 20 L.



8.3 100 mL glass pycnometers

8.3.1 TS 03.01.15

The degrees of equivalence are calculated by linking to the *KCRV* of the key comparison CCM.FF-K4.1.2011, in which three glass pycnometers were used as TS for 100 mL. The participants acting as linking NMIs are CENAM and INMETRO. The TS 03.01.16 used in CCM.FF–K4.1.2011 showed the best performance in terms of the dispersion of the participant's results; therefore, these are the linking data taken from CCM.FF–K4.1.2011 for linking purposes. Similarly, TS 03.01.15 showed the best performance in SIM.M.FF–K4; therefore, these results will be used to define the reference value of this regional comparison for linking purposes.

Table 14 lists the degrees of equivalence of the linking volume measurements on the TS 03.01.16 as determined in the CCM.FF-K4.1.2011 comparison. The *KCRV* value and the associated standard uncertainty of the TS 03.01.16 were: $KCRV$ = 103.091 91 mL, $u(KCRV)$ = 0.000 32 mL

Table 14. Degrees of equivalence for the linking laboratories in CCM.FF-K4.1.2011 comparison.

CCM.FF-K4.1.2011, TS 03.01.16		
	d_i/mL	$U(d_i)$/mL, $k = 2$
CENAM	–0.001 1	0.002 5
INMETRO	–0.000 0	0.000 66

The difference, $d_{i\_\text{link\_CCM}}$, evaluated as weighted mean of the d_i of the linking laboratories was $d_{i\_\text{link\_CCM}}$ = –0.000 1 mL, with a standard uncertainty $u(d_{i\_\text{link\_CCM}})$ = 0.000 32 mL; this result is used to correct the value obtained in this SIM comparison by the linking laboratories. Table 15 shows the results obtained by the linking laboratories in the SIM.M.FF–K4.2017

Table 15. Results of the linking laboratories in SIM.M.FF-K4.1.2017.

SIM.M.FF-K4.1.2017, TS 03.01.15		
	x_i/mL	$u(x_i)$/mL
CENAM	97.811 3	0.001 5
INMETRO	97.810 2	0.000 76

From the results in table 15, by the weighted mean method the value $CRV_{\text{link\_SIM}}$ and the associated standard uncertainty $u(CRV_{\text{link\_SIM}})$ have been evaluated: $CRV_{\text{link\_SIM}}$ = 97.810 4 mL, and $u(CRV_{\text{link\_SIM}})$ = 0.000 68 mL.

In order to link the TS 03.01.15 results to the *KCRV* of the CCM.FF-K4.1.2011, the difference has been calculated as:

$$d_{\mathrm{CRV\_SIM-KCRV}} = CRV_{\mathrm{link\_SIM}} - d_{i\mathrm{\_link\_CCM}} - KCRV$$

$$d_{\mathrm{CRV\_SIM-KCRV}} = 97.810\,4\ \mathrm{mL} - (-0.000\,1\ \mathrm{mL}) - 103.091\,91\ \mathrm{mL} = -5.281\,4\ \mathrm{mL}$$

the standard uncertainty $u(d_{\mathrm{CRV\_SIM-KCRV}})$ can be computed by propagating the uncertainties due to $CRV_{\mathrm{link\_SIM}}$, $d_{i\mathrm{\_link\_CCM}}$ and *KCRV*, according to the following equation:

$$u(d_{\mathrm{CRV\_SIM-KCRV}}) = \sqrt{u(CRV_{\mathrm{link\_SIM}})^2 + u(di_{\mathrm{link\_CCM}})^2 + u(KCRV)^2}$$

$$u(d_{\mathrm{CRV\_SIM-KCRV}}) = \sqrt{(0.000\,68)^2 + (0.000\,32)^2 + (0.000\,32)^2} = 0.000\,82\ \mathrm{mL}$$

To calculate the degrees of equivalence d_i between the SIM laboratories results and the *KCRV*, the following formula is used

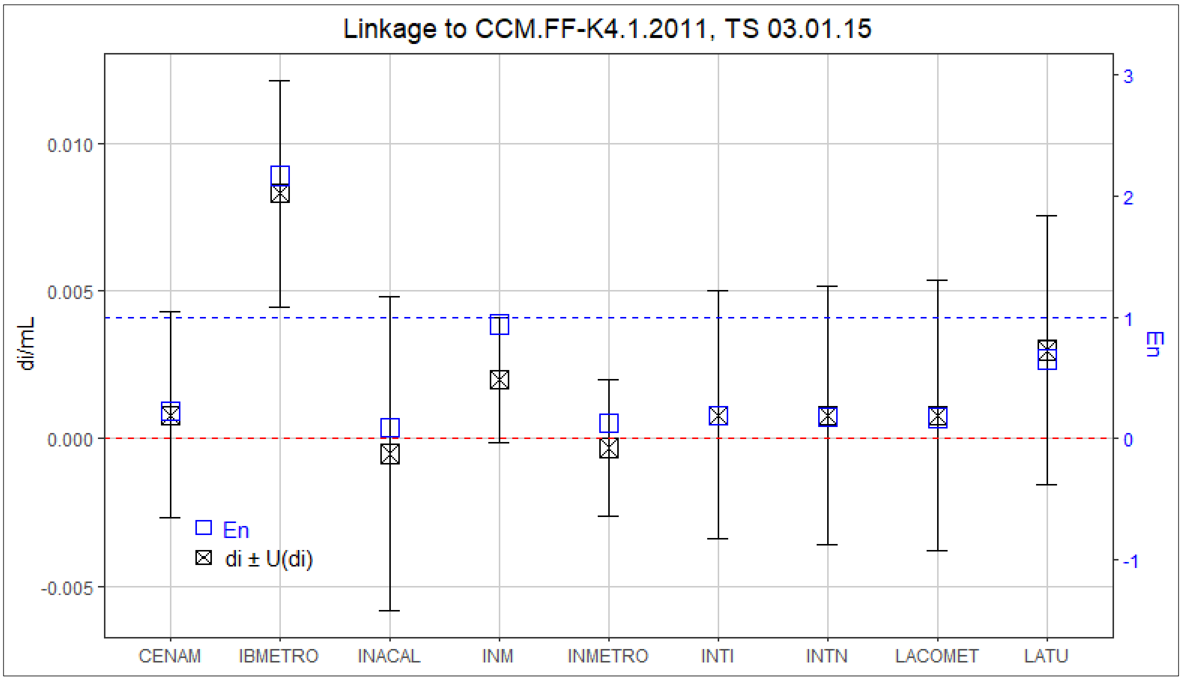
$$d_i = x_i - d_{\mathrm{CRV\_SIM-KCRV}} - KCRV$$

$$U(d_i) = 2\sqrt{u(x_i)^2 + u(d_{\mathrm{CRV\_SIM-KCRV}})^2 + u(KCRV)^2}$$

Table 16. Degrees of equivalence with *KCRV*, and the E_n value.

#	100 mL TS	TS 03.01.15		
		d_i/mL	$U(d_i)$/mL	$\lvert E_{ni} \rvert$
1	CENAM	0.000 79	0.003 5	0.23
2	LACOMET	0.000 79	0.004 6	0.17
3	INM	0.002 00	0.002 1	0.94
4	INACAL	–0.000 50	0.005 3	0.10
5	IBMETRO	0.008 30	0.003 8	2.17
6	INTN	0.000 79	0.004 4	0.18
7	INMETRO	–0.000 30	0.002 3	0.13
8	LATU	0.003 00	0.004 6	0.66
9	INTI	0.000 79	0.004 2	0.19

Graph 3. Degrees of equivalence with *KCRV*, and the E_n value for TS 03.01.15; glass pycnometer for volume of liquids at 100 mL.



8.3.2 TS 03.01.17

Table 17 lists the degrees of equivalence of the linking volume measurements on the TS 03.01.16 as determined in the CCM.FF-K4.1.2011 comparison. The *KCRV* value and the associated standard uncertainty of the TS 03.01.16 were: *KCRV* = 103.091 91 mL, $u(KCRV)$ = 0.000 32 mL

Table 17. Degrees of equivalence for the linking laboratories in CCM.FF-K4.1.2011 comparison.

CCM.FF-K4.1.2011, TS 03.01.16		
	d_i/mL	$U(d_i)$/mL, $k = 2$
CENAM	–0.001 1	0.002 5
INMETRO	–0.000 0	0.000 66

The difference, $d_{i\_\text{link\_CCM}}$, evaluated as weighted mean of the d_i of the linking laboratories was $d_{i\_\text{link\_CCM}}$ = –0.000 1 mL, with a standard uncertainty $u(d_{i\_\text{link\_CCM}})$ = 0.000 32 mL; this result is used to correct the value obtained in this SIM comparison by the linking laboratories. Table 18 shows the results obtained by the linking laboratories in the SIM.M.FF-K4.1.2017.

Table 18. Results of the linking laboratories in SIM.M.FF-K4.1.2017.

SIM.M.FF-K4.1.2017, TS 03.01.17		
	x_i/mL	$u(x_i)$/mL
CENAM	100.982 6	0.001 4
INMETRO	100.980 2	0.000 75

From the results in table 18, by the weighted mean method, the value $CRV_{\text{link\_SIM}}$ and the associated standard uncertainty $u(CRV_{\text{link\_SIM}})$ have been evaluated: $CRV_{\text{link\_SIM}}$ = 100.980 7 mL, and $u(CRV_{\text{link\_SIM}})$ = 0.000 66 mL.

In order to link the TS 03.01.17 results to the *KCRV* of the CCM.FF-K4.1.2011, the difference has been calculated as:

$$d_{\text{CRV\_SIM}-\text{KCRV}} = CRV_{\text{link\_SIM}} - d_{i\_\text{link\_CCM}} - KCRV$$

$$d_{\text{CRV\_SIM}-\text{KCRV}} = 100.980\,7 \text{ mL} - (-0.000\,1 \text{ mL}) - 103.091\,91 \text{ mL} = -2.111\,1 \text{ mL}$$

the standard uncertainty $u(d_{\text{CRV\_SIM}-\text{KCRV}})$ can be computed by propagating the uncertainties due to $CRV_{\text{link\_SIM}}$, $d_{i\_\text{link\_CCM}}$ and *KCRV*, according to the following equation:

$$u(d_{\mathrm{CRV\_SIM-KCRV}}) = \sqrt{u(CRV_{\mathrm{link\_SIM}})^2 + u(di_{\mathrm{link\_CCM}})^2 + u(KCRV)^2}$$

$$u(d_{\mathrm{CRV\_SIM-KCRV}}) = \sqrt{(0.000\,66)^2 + (0.000\,32)^2 + (0.000\,32)^2} = 0.000\,80\ \mathrm{mL}$$

To calculate the degrees of equivalence d_i between the SIM laboratories results and the $KCRV$, the following formula is used

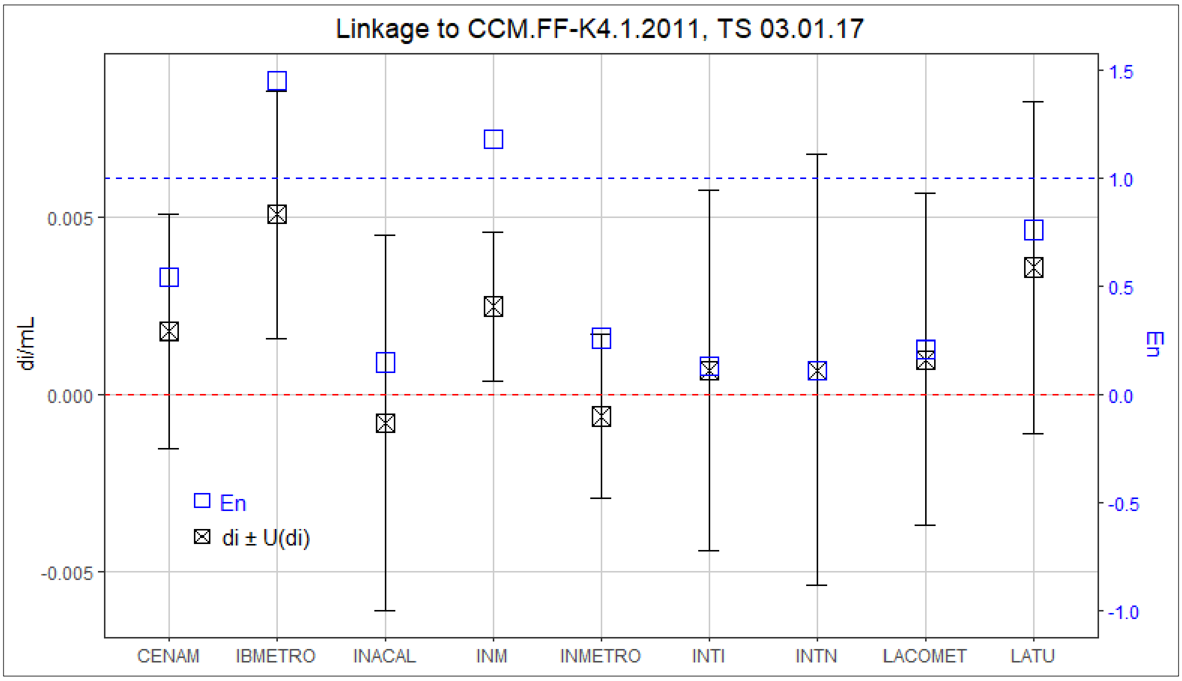
$$d_i = x_i - d_{\mathrm{CRV\_SIM-KCRV}} - KCRV$$

$$U(d_i) = 2\sqrt{u(x_i)^2 + u(d_{\mathrm{CRV\_SIM-KCRV}})^2 + u(KCRV)^2}$$

Table 19. Degrees of equivalence with *KCRV*, and the E_n value.

#	100 mL TS	TS 03.01.17		
		d_i/mL	$U(d_i)$/mL	$\lvert E_{ni} \rvert$
1	CENAM	0.001 79	0.003 3	0.54
2	LACOMET	0.000 99	0.004 7	0.21
3	INM	0.002 49	0.002 1	1.18
4	INACAL	–0.000 81	0.005 3	0.15
5	IBMETRO	0.005 09	0.003 5	1.45
6	INTN	0.000 69	0.006 1	0.11
7	INMETRO	–0.000 61	0.002 3	0.27
8	LATU	0.003 59	0.004 7	0.76
9	INTI	0.00069	0.005 1	0.14

Graph 4. Degrees of equivalence with *KCRV*, and the E_n value for TS 03.01.17; glass pycnometer for volume of liquids at 100 mL.



9. 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 a transfer standard of excellent metrological characteristics (TS 710-05), a common volumetric graduated neck test measure (TS 04) and a glass pycnometers (TS 03.01.15 and 03.01.17); 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, measuring water temperature inside the TSs, the 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 ± $37 \cdot 10^{-6}$ for measurements at 100 mL (TS 03.01.15 and 03.01.17); ± $60 \cdot 10^{-6}$ for overflow type pipettes (TS 710-05) and $168 \cdot 10^{-6}$ for graduated neck test measures (TS 04).

Degrees of equivalence

Looking at the 20 L measurements, all NMIs overlap with each other, and 8 (out of 10), overlap the $KCRV$ for TS 710-05; whereas for TS 04, one (out of 10) NMIs do not overlap the $KCRV$. As for the 100 mL results, 3 measurements (out of 20) do not overlap with the $KCRV$. The only pair of inconsistent results are IBMETRO′s and INMETRO′s, for TS 03.01.15.

CMC analysis of information

Table 20. CMC analysis for calibration of overflow pipettes (TS 710-05)

#	20 L TS	Overflow pipette (TS 710-05)			
		$\|d_i\|$/%	CMC/%	Supported? Y/N	Comments
1	CENAM	0.000 5	0.004	Y	
2	NIST	0.000 1			No CMC entries for overflow devices
3	RECOPE	0.000 5	0.005	Y	
4	INM	0.007 7			No CMCs submitted, yet
5	INACAL	0.010 7	0.007	N	CMC adjustment needed
6	IBMETRO	0.008 9			No CMCs submitted, yet
7	INTN	0.003 3			No CMCs submitted for 20 L artifacts, yet
8	INMETRO	0.001 4	0.002	Y	
9	LATU	0.000 7	0.04	Y	
10	INTI	0.001 2	0.015	Y	

Table 21. CMC analysis for calibration of graduated neck type test measures, by gravimetric method (TS-04).

#	20 L TS	Graduated neck test measure (TS 04)			
		$\|d_i\|$/%	CMC/%	Supported? Y/N	Comments
1	CENAM	0.006 0	0.01	Y	
2	NIST	0.009 5	0.075	Y	
3	RECOPE	0.000 5	0.01	Y	
4	INM	0.001 5			No CMCs submitted, yet
5	INACAL	0.019	0.028	Y	
6	IBMETRO	0.001 5			No CMCs submitted, yet
7	INTN	0.002 5			No CMCs submitted for 20 L artifacts, yet
8	INMETRO	0.009 5			No CMC entries for graduated neck devices
9	LATU	0.015			No CMCs submitted for 20 L graduated neck artifacts by gravimetric method
10	INTI	0.003 5	0.015	Y	

Table 22. CMC analysis for calibration of glass pycnometers (TS 03.01.15 & 03.01.17).

#	100 mL TS	**Glass pycnometers** (average of TSs 03.01.15 and 03.01.17)			
		$\|d_i\|$/%	CMC/%	Supported? Y/N	Comments
1	CENAM	0.001 3	0.004 0	Y	
2	LACOMET	0.000 9	0.005 0	Y	
3	INM	0.002 2			No CMCs submitted, yet
4	INACAL	0.000 7	0.007 0	Y	
5	IBMETRO	0.006 7			No CMCs submitted, yet
6	INTN	0.000 7	0.008 1	Y	
7	INMETRO	0.000 5	0.001 0	Y	
8	LATU	0.003 3	0.005 0	Y	
9	INTI	0.000 7	0.005 0	Y	

10. CONCLUSIONS

- The used transfer standards for SIM.M.FF-K4.1.2017 exhibited good performance all way long, both: in terms of stability and repeatability.
- Measurement results for all transfer standards (TS 710-05, TS 03.01.15 and TS 03.01.17 have been linked to the CCM.FF-K4.1.2011 *KCRV*.
- New CMC entries for some NMIs should consider the information presented herein.

11. REFERENCES

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Annex A

A.1 Results from Measurement Canada, MC

Measurement Canada (MC) is not a designated institute; however, due to its high level of expertise in the field of liquid volume measurement, MC was invited to participate in this comparison exercise. In accordance with MRA rules, its measurement results were not considered for the calculation of the comparison reference value (CRV). Its results and comparison with other NMIs are included in Table A1.

Table A1. Reported results for 20 L TSs (artifact 710-05 and 04)

	20 L TS	**TS 710-05 Overflow pipette**		**TS 04 Graduated neck**	
#		x_i/mL	$u_{\text{nmi}}(x_i)$/mL	x_i/mL	$u_{\text{nmi}}(x_i)$/mL
1	CENAM	19 990.83	0.38	20 004.3	1.9
2	**MC**	19 990.90	0.64	20 009.5	2.5
3	NIST	19 990.94	0.48	20 007.37	2.8
4	RECOPE	19 990.84	0.22	20 005.4	1.40
5	INM	19 989.39	0.35	20 005.18	1.5
6	INACAL	19 988.80	0.80	20 001.7	1.2
7	IBMETRO	19 989.16	0.96	20 005.84	1.7
8	INTN	19 990.28	1.57	20 006.02	1.01
9	INMETRO	19 991.20	1.46	20 007.38	0.95
10	LATU	19 990.80	1.03	20 008.4	1.53
11	INTI	19 990.70	0.41	20 004.8	0.76