Supplementary comparison SIM.M.FF-S12

Final Report
for
Volume of Liquids at 20 L

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CONTENT

1. INTRODUCTION

The National Metrology Laboratory of Costa Rica (LACOMET) and the Refinery Metrology Laboratory of Costa Rica (RECOPE) requested CENAM this Supplementary Comparison to support their CMCs in the measurement of liquid volume.

2. CONDITIONS SELECTED

The participating laboratories determined the volume of water of the Transfer Standard (TS), a stainless steel pipette, of 20 L is able to **deliver**, after a 30 second period of dripping-off at a reference temperature of 20 °C.

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, Mexico	12/10/2016	Manuel Maldonado mmaldona@cenam.mx	Pilot
2	RECOPE, CR	23/12/2016	Esteban Castillo esteban.castillo@recope.go.cr	SIM participant
3	LACOMET,CR	23/01/2017	Luis Damián Rodríguez lrodriguez@lacomet.go.cr	SIM participant
4	CENAM, Mexico	8/06/2017	Manuel Maldonado mmaldona@cenam.mx	Pilot

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

Note: The transportation expenses (Mexico – Costa Rica – Mexico) of the equipment were paid by RECOPE.

When the standard 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.

4. THE TRANSFER PACKAGE

4.1 Transfer Package for 20 L

The 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. 1), which is made of stainless steel, has been designed to:

Figure 1. Photograph of the assembled 20 L transfer standard.

a) Minimize the contribution of the meniscus reading to the volume uncertainty,
b) Minimize the quantity of water drops that remain attached 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.

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 cubic coefficient of expansion for the stainless steel used to make the TS is $(47.7 \pm 2.0) \times 10^{-6}\ ^{o}C^{-1}$; the uncertainty is expressed as standard uncertainty.

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. The pilot laboratory performed 6 measurements.

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

		Date of test				
		1	2	3	4	5
Measurements per day		Reception and inspection	Experiment al set-up and Acclimatization	x_1	x_6	Packaging of the TS´s for shipment to next NMI.
				x_2	x_7	
				x_5	x_{10}	
			$x = \frac{1}{n}\sum_{i=1}^{n} x_i$ x_i are individual results referenced to 20° C.			

6. EXPERIMENTAL PROCEDURES

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

	Weighing*	**Water****	**De-aerated water?**	**Density formula**
CENAM	DS	IE + O	No	Tanaka
RECOPE	DS	IE + O +D	No	Tanaka
LACOMET	SS	1D	No	Tanaka

***Weighing:** *DS*: Double substitution; *SS*: single substitution
****water:** IE: Ion exchange; O: Inverse osmosis; 1D: single distillation

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. 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	RECOPE	LACOMET
$(t_d - 20)$/°C	2.3	0.21	0.62
$(t_w - t_a)$/°C	–1.0	–0.23	0.51

7. RESULTS

7.1 Stability of the TSs

CENAM as the pilot laboratory tested the artifact before and after the comparison. The results of the testing are given in tables 5. Initial test values correspond to the official measurement results of CENAM and are taken for the calculation of the CRV.

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

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, $k = 2$	
12/10/2016	19 989.02 ± 0.68	09/06/2017	19 989.24 ± 0.85	0.22

No substantial drift was observed on the 20 L 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.

7.2 Results reported by the participants

Tables 6 show the results and standard uncertainties as reported by the participants.

Table 6. Reported results for 20 L TSs.

20 L TSs	**TS 710-04**	
	x_i/mL	$u(x_i)$/mL
CENAM	19 989.02	0.34
RECOPE	19 988.82	0.37
LACOMET	19 988.58	0.33

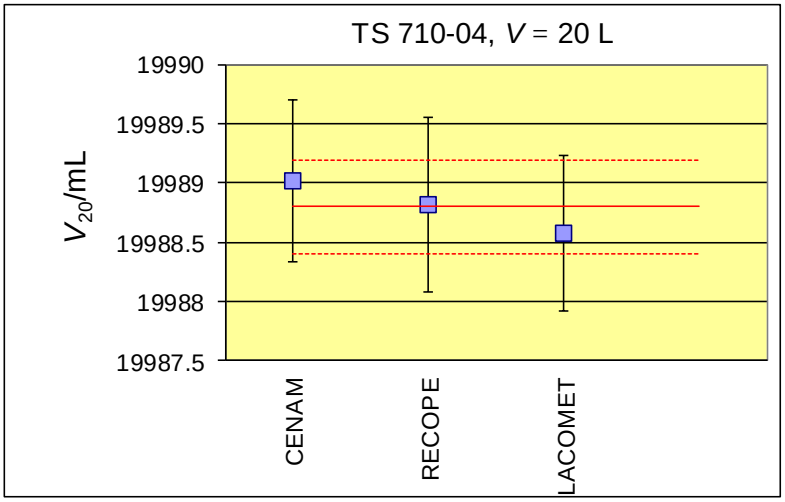
8. COMPUTATION OF THE COMPARISON REFERENCE VALUES

The CRV for volume of liquids at 20 L has been calculated by applying the ***"weighted mean"*** method as suggested by Cox [7]. Table 7 shows the calculations.

Table 7. Consistency check and computation of SIM.M.FF-S12 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	19 989.02	0.34	172 915.398	8.650 519	0.414 3
RECOPE	19 988.82	0.37	146 010.373	7.304 601	0.002 6
LACOMET	19 988.58	0.33	183 549.862	9.182 736	0.449 12
		Σ	502 475.633	25.137 857	0.866 02
			x_{ref}/mL	19 988.80	$\chi^2(0.05,2)$ = 5.99
			$u(x_{ref})$/mL	0.20	pass

Figure 2. Measurement results for TS 710-04. Horizontal solid bold line represents the CRV, calculated according to Cox method. The Uncertainties are expressed with $k = 2$.



9. DETERMINATION OF THE DEGREES OF EQUIVALENCE (DoE)

Tables 8. Degree of equivalence for Volume of Liquids at 20 L

TS 710–04	$\frac{d_i}{x_{ref}} \cdot 10^6$	$\frac{U(d_i)}{x_{ref}} \cdot 10^6$	$E_n(x_i)$		CENAM		RECOPE		LACOMET	
NMI					$\frac{d_{ij}}{\bar{x}_{ij}} \cdot 10^6$			$\frac{U(d_{ij})}{\bar{x}_{ij}} \cdot 10^6$		
CENAM	11	28	0.28				–10	50	–22	47
RECOPE	1	31	0.022		10	50			–12	50
LACOMET	–11	26	–0.43		22	47	12	50		

10. CMC CONSISTENCY CHECK

In order to judge 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 9. Consistency check for CMC entries for volume of liquids at 20 L.

NMI	U_{CMCs}	$U_{SIM.M.FF-S12}$	$\frac{d_i}{x_{ref}}$	Are the CMCs supported by SIM.M.FF-S12
	%	%	%	
CENAM	0.004 0	0.003 4	0.001 1	yes
RECOPE	0.005 0	0.003 9	0.000 09	yes
LACOMET	0.020 0	0.003 4	–0.001 1	yes

11. CONCLUSIONS

i. SIM.M.FF-S12 for Volume of Liquids at 20 L was conducted during 2016 – 2017.

ii. No discrepant measurements were distinguished on the 20 L artifact. The largest difference between two NMIs was 0.002 2 %.

12. REFERENCES

1. Tanaka, M., et. al; *Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports*, Metrologia, 2001, 38, 301-309.
2. Bettin, H., and Spieweck, F., *Die Dichte des Wassers als Funktion der Temperatur nach Einfuehrung der Internationalen Temperaturskala von 1990*, PTB-Mitteilungen, 100, 1990, 195-196.
3. Patterson, J. B. and Morris, E. C., *Measurement of Absolute Water Density, 1℃ to 40℃*, Metrologia, 31, 1994, 277-288.
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5. JCGM 100:2008, *Guide to the expression of uncertainty in Measurement*.
6. BIPM, *International temperature scale of 1990*, Part 2. Techniques and thermometers traceable to the international temperature scale of 1990; Section 16. Industrial platinum resistance thermometers.
7. Cox M., *The evaluation of key comparison data*; Metrologia, 2002, 39, 589-595.

Appendix A
UNCERTAINTY CONTRIBUTIONS

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

20 L - contributions in mL -	CENAM	RECOPE	LACOMET
Balance	0.056	0.002 1	0.095
Weights	0.007	0.016	0.011
water temperature (calibration)	0.33	0.025	0.31
Temperature gradients			
water density	0.052	0.36	
air temperature	0.008	0.011	0.026
Relative humidity	0.004	0.000	0.000 6
Ambient pressure	0.001	0.002	0.005
Artifact temperature			
Thermal expansion coefficient	0.055	0.003	0.025
Leaks	0.12		
Evaporation			
Clingage			
Repeatability	0.023	0.032	0.016
Others			
combined uncertainty; $u(V_{20})$/mL	0.34	0.37	0.33
expanded uncertainty; $U(V_{20})$/mL	0.68 (k = 2)	0.77 (k = 2.08)	0.68 (k = 2.07)

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 0.01 °C/$u(t)$ = 0.2 °C	Druck DPI 740 1 Pa/$u(p)$ = 4.5 Pa	Vaisala HM34 0.01 %/$u(hr)$ = (0.25 – 0.55) %	CENAM
RECOPE	Mettler XP64003L 64 kg/0.005 g/	Troemner + Sartorius F1	Vaisala PTU 300 0.01 °C/0.13 °C	Vaisala PTU 300 0.02 hPa/0.02 hPa	Vaisala PTU 300 0.01 %/0.8 %	LACOMET
LACOMET	Mettler XP32003L 30 kg/0.005 g/0.091 g	Sartorius F1+F2	Vaisala PTU 200 0.1 °C/0.3 °C	Vaisala PTU 200 0.1 hPa/0.1 hPa	Vaisala PTU 200 1 %/2 %	LACOMET