Results of the second round of International Comparison for volume of Liquids at 20 L and 100 mL

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Abstract

By agreement at the 10th WGFF meeting, the international comparison, for Volume of Liquids at 20 L and 100 mL, was performed during 2012 – 2014. Specially designed stainless steel pipettes were used as transfer standards for 20 L, whereas commercially available pycnometers were used for 100 mL. Only one measurement result, out of 39, was qualified as non-consistent. The average degree of equivalence $\bar{d}_{i,j}$, for artifacts at 20 L (TS 710-04 and 710-05) resulted in 0.000 1 % and 0.000 44 %, respectively. As for the 100 mL artifacts, the average degree of equivalence $\bar{d}_{i,j}$, for artifacts TS 03.01.12, 03.01.16 and 03.01.17 resulted in 0.000 54 %, 0.000 17 % and 0.001 1 %, respectively.

1. Introduction

Back in 2003, the first version of the International Comparison for Volume of Liquids at 20 L and 100 mL (under the umbrella of the International Committee for Weights and Measures) included 8 institutes, from eight economies; including participants from SIM, EURAMET and APMP. This second version of the International Comparison included 10 institutes, from 10 economies; six of which had already participated in the first round (CENAM/Mexico, NIST/USA, MC/Canada, SP/Sweden, INRIM/Italy and INMETRO/Brazil.

The transfer standards that were used for the second version of the Volume of Liquids at 20 L and 100 mL were the same as those for the first version. This time however, instead of using three artifacts for 20 L, only two stainless steel pipettes (FV-04 and FV-05) were used; similarly, three 100 mL pycnometers (03.01.12, 03.01.16 and 03.01.17) instead of the six pycnometers used back in 2003. Of course, all artifacts were re-manufactured in order to slightly change its corresponding volume (ether to contain or to deliver).

It is intended that at least one participating institute from each Regional Metrology Organization could, in the near future, lead the corresponding and subsequent, RMO Key Comparison; using the same, but slightly modified, transfer standards. These RMO Key Comparisons will allow linking any RMO participant to the KCRV.

Measurements from KEBS were not included into the calculation of the Reference Value because of the lack of the uncertainty statements for all of the artifacts.

2. Participants

#	Participant	Date	Contact	Remarks
1	CENAM, México	03/2012	Roberto Arias	Pilot
2	NIST, USA	05/2012	John Wright	SIM participant
3	MC, Canada	06/2012	Christian Lachance	SIM participant
4	IPQ, Portugal	07/2012	Elsa Batista	EURAMET participant
5	VSL, Netherlands	08/2012	Erik Smits	EURAMET participant
6	SP, Sweden	09/2012	Olle Penttinen	EURAMET
7	INRIM, Italy	10/2012	Andrea Malengo	EURAMET pivot
8	NIM, China	01/2013	Wang Jintao	APMP pivot
9	KEBS, Kenya	04/2013	Dominic Ondoro	AFRIMET participant
10	INMETRO, Brazil	02/2014	Dalni Malta	SIM participant

Table 1. List of participants for Comparison on Volume of Liquids at 20 L and 100 mL.

3. Conditions selected

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

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.

Fig. 1. Image of the 20 L transfer standard

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

a) Minimize the contribution of the meniscus reading to the volume uncertainty,
b) 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 $(47.7 \pm 2.0) \times 10^{-6}$ ºC^{-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. 2). 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 $(9.9 \pm 1) \times 10^{-6}$ °C^{-1}.

Fig. 2. Image of the 100 mL transfer standards

5. Experimental procedures

	Weighing*		Water**	De-aerated water?	Density formula
	20 L	100 mL			
CENAM	DS	DR	IE + O	No	Tanaka et al[1]
NIST	DR		O	No	Patterson & Morris[2]
MC	SS		1D	No	Tanaka et al
IPQ	SS	SS	IE + O	No	Tanaka et al
VSL	DS	DS	DM+2D	No	Bettin & Spieweck[3]
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

Table 2. Summary of the experimental procedure employed at the different NMIs

***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

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.

6. Results

6.1 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 3 and 4. Initial tests values correspond to the official measurements results of CENAM and are taken for the calculation of the KCRV.

20 L	date	initial	date	final	$\|\Delta V\|$/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 3. Stability of the 20 L TSs, according to the measurement results obtained at the pilot laboratory.

100 mL	date	initial	date	final	$\|\Delta V\|$/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

Table 4. Stability of the 100 mL TSs, according to the measurement results obtained at the pilot laboratory.

No substantial drift was observed either on the 20 L TSs nor on the 100 mL TSs; the initial and final measurements at the pilot NMI showed to be 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 neither NIST nor MC tested the 100 mL artifacts, the technical contacts noted that they are not including calibration services of glassware in their corresponding CMC list. Therefore, 20 L TSs were tested by 10 participants, whereas 100 mL TSs by 8 NMIs.

6.2 Results reported by the participants

Tables 5 and 6 show the results and standard uncertainties as reported by the participants.

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
MC	19 990.45	0.75	19 993.24	0.75
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
KEBS	19 978.13		20 007.64	
INMETRO	19 991.05	0.20	19 993.81	0.20

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
KEBS	100.407 0		100.955 1		100.017 3	
INMETRO	99.643 3	0.000 48	103.091 9	0.000 46	100.595 5	0.000 44

Tables 5 & 6. Reported results for 20 L and 100 mL TSs.

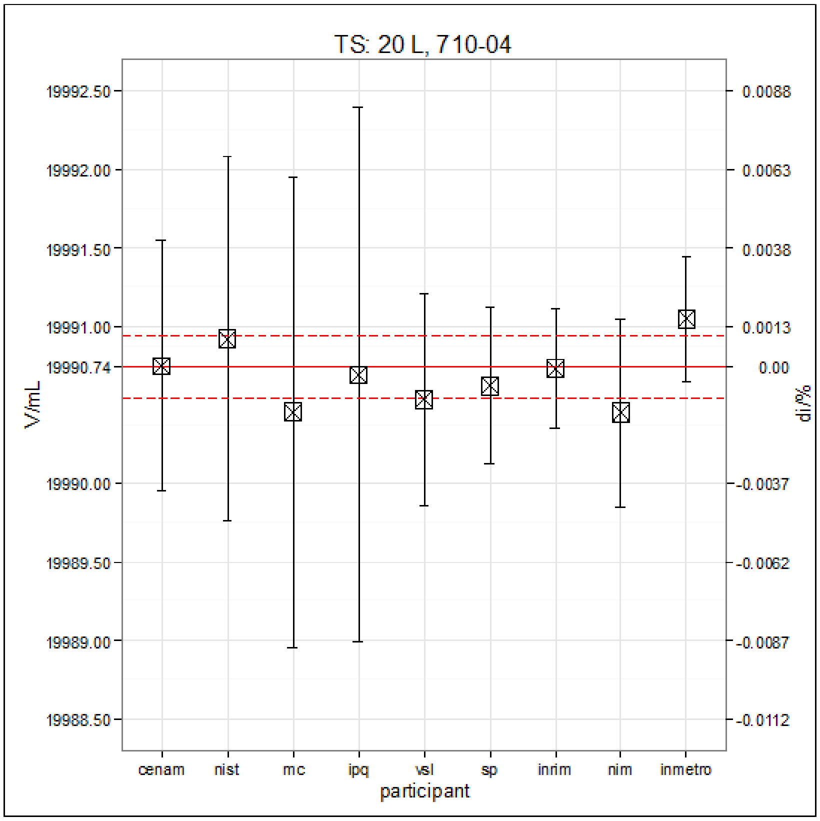
7. Computation of the key comparison reference values

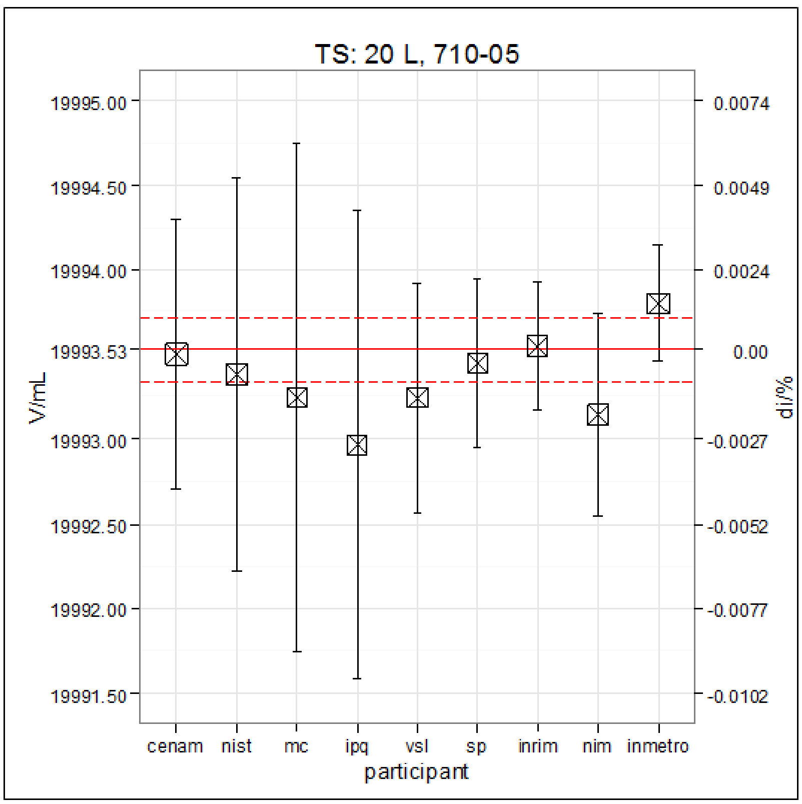
The KCRV for volume of liquids at 20 L and 100 mL has been calculated by applying the ***"weighted mean"*** method as suggested by Cox[4]. Tables 7 – 11 show the calculations.

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	124 942.17	6.25	0.000
NIST	19 990.92	0.58	59 426.04	2.97265161	0.093
MC	19 990.45	0.75	35 538.58	1.77777778	0.152
IPQ	19 990.69	0.85	27 668.78	1.38408304	0.003
VSL	19 990.53	0.34	172 928.46	8.65051903	0.390
SP	19 990.62	0.25	319 849.89	16	0.248
INRIM	19 990.73	0.19	553 759.75	27.700831	0.007
NIM	19 990.45	0.30	222 116.10	11.1111111	0.960
INMETRO	19 991.05	0.20	499 776.14	25	2.292
		Σ	2016005.9	100.846974	4.145
			x_{ref}/mL	19 990.74	$\chi^2_{0.05,8}$ = 15.5
			$u(x_{ref})$/mL	0.10	**pass**

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	124 959.40	6.25	0.000
NIST	19 993.39	0.58	59 433.37	2.97265161	0.040
MC	19 993.24	0.75	35 543.55	1.77777778	0.118
IPQ	19 992.97	0.69	41 993.21	2.10039908	0.600
VSL	19 993.25	0.34	172 951.95	8.65051903	0.568
SP	19 993.45	0.25	319 895.18	16	0.045
INRIM	19 993.55	0.19	553 837.95	27.700831	0.065
NIM	19 993.14	0.3	222 146.03	11.1111111	1.428
INMETRO	19 993.81	0.17	691827.2	34.6020761	2.678
		Σ	2222587.84	111.165366	5.996
			x_{ref}/mL	19 993.53	$\chi^2_{0.05,8}$ = 15.5
			$u(x_{ref})$/mL	0.095	**pass**

Tables 7 & 8. Consistency check and computation of KCRV for TSs 710-04 and 710-05





Figs. 3 & 4. Measurement results for 20 L artifacts.

TS 03.01.12	x_i/mL	$u(x_i)$/mL	$x_i/u(x_i)^2$	$1/u(x_i)^2$	$(x_i - x_{ref})^2/u(x_i)^2$
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
			$u(x_{ref})$/mL	0.000 33	**pass**

Table 9. Consistency check and computation of KCRV for TS 03.01.12.

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**

Table 10. Consistency check and computation of KCRV for TS 03.01.16.

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

Table 11. Consistency check and computation of KCRV for TS 03.01.17.

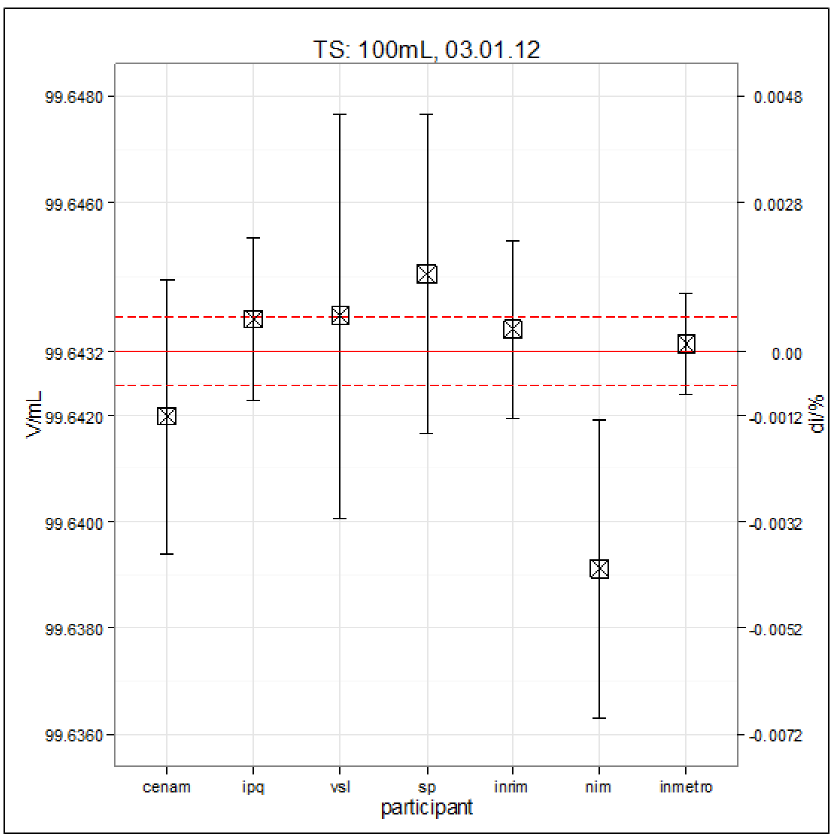
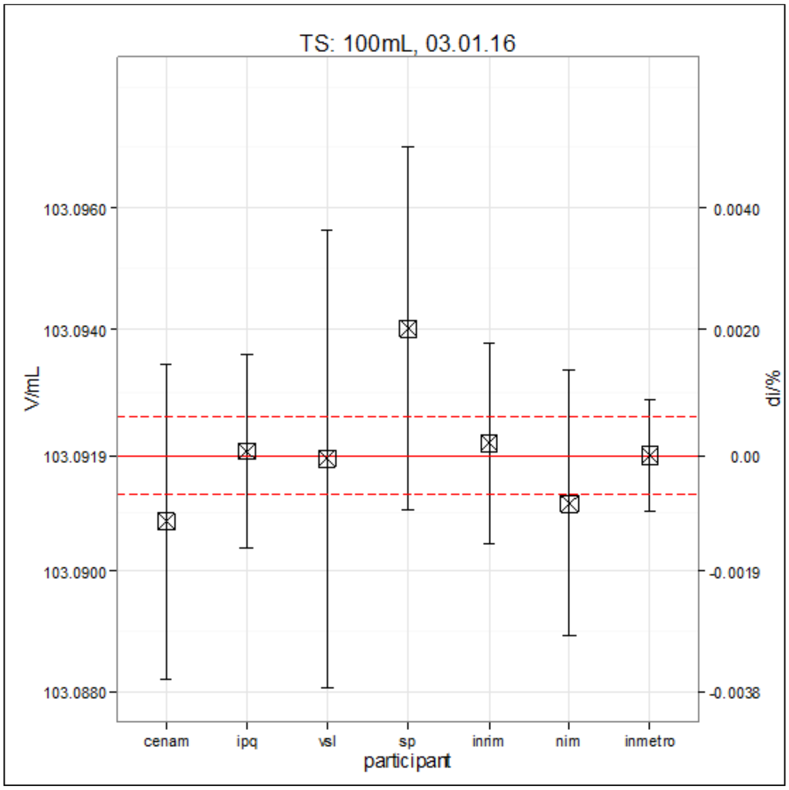
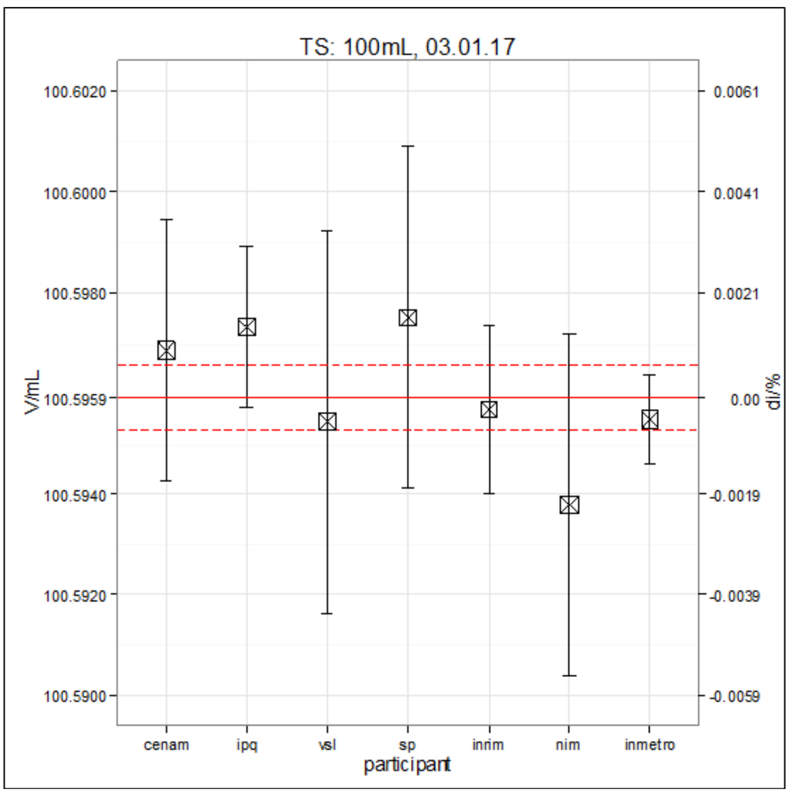


Fig. 5. Measurement results for 20 L artifacts.





Figs. 6 & 7. Measurement results for 100 mL artifacts.

8. Conclusions

i. The International Comparison for Volume of Liquids at 20 L and 100 mL was conducted during 2012 – 2014; its execution 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. The comparison project was piloted by CENAM. Ten institutes tested the two 20 L transfer standards, whereas 8 tested the three 100 mL pycnometers.

iii. No discrepant measurements were distinguished on the 20 L artifacts. The largest difference between two participants 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 44 %, 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.

9. Acknowledgments

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