Final Report
on

SIM / ANDIMET Supplementary Comparison
for
Volume of Liquids at 100 mL and 100 µL

SIM.M.FF-S7

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Volume Comparison at 100 mL – Calibration of Pycnometers

Volume Comparison at 100 µL – Calibration of Piston Pipettes

July 06, 2016

Measurements Conducted January 2012 to December 2013

CONTENT

1. INTRODUCTION

During the coordination meeting of ANDIMET, held within the framework “FOMENTO COORDINADO DE LA INFRAESTRUCTURA DE LA CALIDAD EN LA REGIÓN ANDINA, CAN-PTB” in La Paz, Bolivia, on 31 May and 1 June 2011, it was agreed to conduct some comparisons between the National Metrological Institutes (NMIs) of Andean Region, which includes a comparison in the magnitude of volume of liquids, in order to compare the performance of volume measurements of the participating laboratories from ANDIMET – Bolivia, Colombia, Ecuador and Peru. Also it was decided to include Costa Rica, Uruguay and Paraguay.

The organization of the comparison was coordinated by the national metrology institute of Bolivia (IBMETRO) as the pilot laboratory, with the technical assistance of the CENAM, whom also performed measurements of the pycnometers and pipettes at the beginning and the end of the round of measurements between different participating NMIs.

The main objective of the comparison is to provide evidence to support the calibration and measurement capabilities (CMCs) of the participating laboratories from ANDIMET and the other participating countries using two pycnometers of 100 mL and two piston pipettes of 100 µL.

Before starting the comparison, a protocol based on BIPM guidelines was approved by all participants during the inception meeting which took place in March 2012 in La Paz, Bolivia. The comparison started in January 2012 and ended in October 2013.

2. PARTICIPANTS

Each laboratory was responsible for receiving the transfer packages, testing and sending them to the next participant according to the schedule given in Table 1. The CENAM laboratory had two dates of measurements in order to verify the stability of the travelling standards.

Table 1. NMI participants and circulation timetable of the equipment.

Laboratory	Acronym	Country	Contact person	Arrival date
Centro Nacional de Metrología	CENAM	Mexico	Sonia Trujillo / Manuel Maldonado	2012-01-15
Instituto Boliviano de Metrología	IBMETRO	Bolivia	Maria Vega / Elisa Santalla	2012-03-20
Laboratorio Tecnológico del Uruguay	LATU	Uruguay	Andrea Sica	2012-04-26
Instituto Nacional de Tecnología, Normalización y Metrología	INTN	Paraguay	Diana Cantero	2012-08-27
Instituto Ecuatoriano de Normalización	INEN	Ecuador	Manuel Salazar	2012-11-12
Instituto Nacional de Defensa de la Competencia y de la Protección de la Propiedad Intelectual	INDECOPI	Peru	Abed Morales	2013-01-16
Instituto Nacional de Metrología	INM	Colombia	Pablo Solano	2013-03-08
Laboratorio Costarricense de Metrología	LACOMET	Costa Rica	Luis Damián Rodríguez	2013-05-20
Centro Nacional de Metrología	CENAM	México		2013-10-04

3. TRANSFER STANDARDS

The transfer standards (TS) selected to be used in this comparison are two commercially available glass pycnometers type Gay-Lussac with a nominal volume of 100 mL (see Figure 1) and two air displacement single-channel fixed piston pipettes of 100 µL nominal volume (see Figure 2).

The pycnometers are made of borosilicate glass with a cubic thermal expansion coefficient of 9.9×10^{-6}/°C [1].

The piston pipettes need to be attached to a removable plastic tip in order to aspirate the liquid. The piston pipettes with the tips were supplied to all participants to perform the measurements. The cubic thermal expansion coefficient of the piston pipettes is taken into account with the value of 2.4×10^{-4}/°C in this comparison.

The serial numbers of the 4 transfer standards used in this comparison are the following:

Pycnometer Gay-Lussac of 100 mL, 11.04.08

Pycnometer Gay-Lussac of 100 mL, 11.04.09

Single-channel piston-operated pipette with air displacement, fixed volume of 100 µL, 153603A

Single-channel piston-operated pipette with air displacement, fixed volume of 100 µL, 153607A

Figure 1. Pycnometers of 100 mL

Figure 2. Piston pipettes of 100 µL

4. MEASUREMENT PROCEDURE

Each participating laboratory determined the volume of each pycnometer in a way that 10 measurements were performed for each artifact.

In the case of the piston pipettes, two events of calibration (10 measurements for each calibration) were registered by each piston pipette.

4.1 Experimental method

During the inception meeting of the comparison, all the participating NMIs agreed to apply a gravimetric method to determine the volume of the transfer standards, which was defined in the protocol.

The laboratories used direct weighing or single substitution to determine the amount of water that the pycnometers contain and piston pipettes deliver, applying a reference temperature of 20 ºC according to ISO 4787 [1], and ISO 8655 [2], see equation (1):

$$V_{20} = (I_{\mathrm{L}} - I_{\mathrm{E}}) \times \frac{1}{\rho_{\mathrm{W}} - \rho_{\mathrm{A}}} \times \left(1 - \frac{\rho_{\mathrm{A}}}{\rho_{\mathrm{B}}}\right) \times \left[1 - \gamma (t - 20)\right] \qquad (1)$$

Where:

V_{20}/mL	volume at 20 ºC in mL (pycnometers) or µL (piston pipettes)
I_{l}/g	weighing result of the recipient full of liquid
I_{E}/g	weighing result of the empty recipient
ρ_{W}/(g/mL)	water density, at the calibration temperature *t* in ºC, Tanaka density formula [3],
ρ_{A}/(g/mL)	air density
ρ_{B}/(g/mL)	density of masses used during measurement (substitution) or during calibration of the balance
γ/°C^{-1}	cubic thermal expansion coefficient of the borosilicate glass or the piston pipette
t/°C	water temperature

The type of water used by each participant was obtained by different processes. A summary is given in Table 2. The formulation of Tanaka et al [3] was used for all participants as the reference equation for the density of water. The conductivity was determined by the majority of the laboratories.

Table 2. Summary of the experimental procedure employed and the type of water used at the different NMIs

NMI	**Weighing** 100 mL and 100 µL	**Type of water**	**Density formula**	**Conductivity** (µS/cm)
CENAM	Direct weighing	De-ionized + inverse osmosis	Tanaka	2
IBMETRO	Direct weighing	Distilled + de-ionized	Tanaka	6.07
LATU	Direct weighing	De-ionized + inverse osmosis	Tanaka	1.6
INTN	Direct weighing	-	Tanaka	-
INEN	Direct weighing	De-ionized	Tanaka	0.078
INDECOPI	Direct weighing	Distilled	Tanaka	1
INM	Direct weighing	Bi-distilled	Tanaka	4
LACOMET	Single substitution/ Direct weighing	Bi-distilled	Tanaka	0.80

4.2 Equipment

The participants reported their equipment used for calibration and the respective traceability on a prepared template form. Annex A describes the equipment and traceability information for measurements at 100 mL and 100 µL.

5. MEASUREMENT RESULTS

5.1 Stability of the transfer standards

Two different measurements of the transfer standard were performed by CENAM, at the beginning and end of the round of measurements between the different participating NMIs in order to verify the stability of the standards. The results of the testing are given in Tables 3 and 4.

Initial test values of the 100 mL TSs correspond to the official measurement results of CENAM and are taken for the calculation of the comparison reference value, *CRV*.

In the case of the piston pipettes, the two events of calibration, i.e. the initial and final measurements, were taken for the calculation of the *CRV*

Table 3. Stability of the 100 mL TSs, according to the measurement results obtained at CENAM

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 11.04.08	03/2012	99.825 8 ± 0.002 6	01/2014	99.825 9 ± 0.002 6	0.000 1
TS 11.04.09		100.514 5 ± 0.002 6		99.514 6 ± 0.002 6	0.000 1

Table 4. Stability of the 100 µL TSs, according to the measurement results obtained at CENAM

100 µL	date	initial	date	final	$\|\Delta V\|$/µL
		$(x_i \pm u(x_i))$/µL, k = 2		$(x_i \pm u(x_i))$/µL, k = 2	
TS 153603A	02/2012	100.01 ± 0.20	10/2013	99.98 ± 0.20	0.03
TS 153607A		99.88 ± 0.20		99.90 ± 0.20	0.02

No substantial drift was observed neither with the 100 mL TSs nor the 100 µL TSs; the initial and final measurements performed at CENAM showed to be consistent with each other, within the uncertainty. Therefore, no additional contribution of uncertainty due to drift will be included when calculating the degrees of equivalence.

5.2 Results reported by the participants

Table 5 shows the results and standard uncertainties as reported by the participants for the pycnometers, as well as the comparison reference value *CRV* calculated for each pycnometer using the results submitted by the participants. Table 6 shows the results and standard uncertainties as reported by the participants for the piston pipettes. The laboratories performed two calibration exercises for each piston pipette in order to demonstrate the reproducibility of their measurements to these artifacts. It should be noted that INEN sent results only for one calibration of each piston pipette.

Table 5. Reported results by the participants for the 100 mL pycnometers

100 mL TS	Pycnometer 11.04.08		Pycnometer 11.04.09	
	x_i/mL	$U(x_i)$/mL	x_i/mL	$U(x_i)$/mL
CENAM	99.825 9	0.002 6	100.514 5	0.002 6
IBMETRO	99.827 6	0.003 4	100.516 0	0.003 4
LATU	99.822 7	0.003 5	100.512 2	0.003 5
INTN	99.823 0	0.007 8	100.511 8	0.005 8
INEN	99.814	0.008	100.504 6	0.009
INDECOPI	99.825 4	0.006 4	100.515 3	0.006 2
INM	99.825 0	0.007 2	100.499 0	0.007 2
LACOMET	99.823 1	0.002 5	100.512 0	0.002 4

	CRV/mL	$U(CRV)$/mL	*CRV*/mL	$U(CRV)$/mL
CRV	99.824 4	0.001 3	100.513 3	0.001 3
Method	Weighted mean		Weighted mean	

Table 6. Reported results by the participants for the 100 µL piston pipettes

100 µL TS	100 µL Piston pipette 153603A				100 µL Piston pipette 153607A			
	Calibration 1		Calibration 2		Calibration 1		Calibration 2	
	V/µL	*U*/µL	*V*/µL	*U*/µL	*V*/µL	*U*/µL	*V*/µL	*U*/µL
CENAM	99.69	0.20	99.67	0.20	99.57	0.20	99.58	0.20
IBMETRO	99.225	0.055	99.128	0.055	99.207	0.033	99.030	0.033
LATU	100.16	0.56	100.07	0.45	100.11	0.47	99.88	0.32
INTN	100.1	0.2	100.1	0.2	100.0	0.1	99.9	0.1
INEN	98.92	0.30	--	--	98.71	0.23	--	--
INDECOPI	100.11	0.14	100.03	0.12	99.988	0.098	100.00	0.11
INM	99.769	0.162	99.372	0.167	99.120	0.117	99.054	0.078
LACOMET	99.79	0.51	99.77	0.56	99.49	0.63	99.63	0.49

Calibrations of piston pipettes with air cushion at various altitudes have a significant influence on the measuring results. To achieve the comparability of the calibration results, corrections for the altitude must be made [4].

The change in volume that results from the calibration at a location X2 (with the atmospheric pressure p_{X2}) compared to a location X1 (with the atmospheric pressure p_{X1}) is determined by applying the following formula [4]:

$$\Delta V = -V_C \cdot \rho_W \cdot g \cdot h_W \cdot \left(\frac{1}{p_{X2} - \rho_W \cdot g \cdot h_W} - \frac{1}{p_{X1} - \rho_W \cdot g \cdot h_W} \right) \qquad (2)$$

Where,

ΔV/µL	Volume change that results in the calibration at a location X1 over a location X2
V_C/µL	Volume of the air cushion
g/(m/s^2)	Gravitational acceleration
h_W/m	Lifting height of the liquid column in the pipette tip
ρ_W/(kg/m^3)	Water density
p_{X1}/Pa	Atmospheric pressure at location X1
p_{X2}/Pa	Atmospheric pressure at location X2

The results in Table 6 were corrected for the standard atmospheric pressure of 1 013.25 hPa using equation 2, obtaining the results shown in Table 7.

The values of h_w/m = 0.030 and V_C/µL = 437 for the air pressure correction were obtained from the piston pipette manufacturer (Eppendorf).

Table 7. Volume measurement results of the piston pipettes corrected for reference condition (p = 1 013.25 hPa)

100 µL TS	**Piston pipette 153603A**				**Piston pipette 153607A**			
	Calibration 1		Calibration 2		Calibration 1		Calibration 2	
	V/µL	U/µL	V/µL	U/µL	V/µL	U/µL	V/µL	U/µL
CENAM	100.01	0.20	99.98	0.20	99.88	0.20	99.90	0.20
IBMETRO	99.884	0.055	99.785	0.055	99.867	0.033	99.689	0.033
LATU	100.15	0.56	100.06	0.45	100.11	0.47	99.88	0.32
INTN	100.1	0.2	100.1	0.2	100.0	0.1	99.9	0.1
INEN	99.39	0.30	--	--	99.18	0.23	--	--
INDECOPI	100.15	0.14	100.08	0.12	100.03	0.098	100.05	0.11
INM	100.205	0.162	99.808	0.167	99.559	0.117	99.493	0.078
LACOMET	99.98	0.51	99.96	0.56	99.68	0.63	99.82	0.49

The determination of the volume change for the piston pipettes is shown in the Tables 8 to 11.

Table 8. Volume change determination for piston pipette 153603A, calibration 1

Piston pipette 153603A					
100 µL TS	Calibration 1				
	ρ_w/(kg/m^3)	p_{X2}/Pa	ΔV/µL	V/µL	V_{corr}/µL
CENAM	998.692 3	81 246	–0.315	99.69	100.01
IBMETRO	998.154 4	66 800	–0.659	99.225	99.884
LATU	998.200 5	101 825	0.006	100.16	100.15
INTN	998.54	101 026	–0.004	100.1	100.1
INEN	997.894 8	74 179	–0.467	98.92	99.39
INDECOPI	998.278	97 882	–0.045	100.11	100.15
INM	998.378	75 500	–0.436	99.769	100.205
LACOMET	997.99	88 026	–0.193	99.79	99.98

Table 9. Volume change determination for piston pipette 153603A, calibration 2

Piston pipette 153603A					
100 µL TS	Calibration 2				
	ρ_w/(kg/m^3)	p_{X2}/Pa	ΔV/µL	V/µL	V_{corr}/µL
CENAM	998.656 8	81 207	–0.316	99.67	99.98
IBMETRO	998.081 0	66 860	–0.658	99.128	99.785
LATU	998.181 9	101 825	0.006	100.07	100.06
INTN	998.55	101 092	–0.003	100.1	100.1
INEN	--	--	--	--	--
INDECOPI	998.218	97 304	–0.053	100.03	100.08
INM	998.378	75 500	–0.436	99.372	99.808
LACOMET	998.05	88 191	–0.190	99.77	99.96

Table 10. Volume change determination for piston pipette 153607A, calibration 1

Piston pipette 153607A					
100 µL TS	Calibration 1				
	ρ_w/(kg/m^3)	p_{X2}/Pa	ΔV/µL	V/µL	V_{corr}/µL
CENAM	998.840	81 505	–0.310	99.57	99.88
IBMETRO	998.175 2	66 800	–0.659	99.207	99.867
LATU	998.206 7	101 668	0.004	100.11	100.11
INTN	998.54	101 081	–0.003	100.0	100.0
INEN	998.101 7	74 344	–0.463	98.71	99.18
INDECOPI	998.274	97 775	–0.046	99.99	100.03
INM	998.317	75 400	–0.439	99.120	99.559
LACOMET	998.00	88 031	–0.192	99.49	99.68

Table 11. Volume change determination for piston pipette 153607A, calibration 2

Piston pipette 153607A					
100 µL TS	Calibration 2				
	ρ_w/(kg/m^3)	p_{X2}/Pa	ΔV/µL	V/µL	V_{corr}/µL
CENAM	998.728	81 125	–0.318	99.58	99.90
IBMETRO	998.175 2	66 800	–0.659	99.030	99.689
LATU	998.192 3	101 668	0.004	99.88	99.88
INTN	998.49	100 758	–0.007	99.9	99.9
INEN	--	--		--	--
INDECOPI	998.182	97 285	–0.053	100.00	100.05
INM	998.317	75 400	–0.439	99.054	99.493
LACOMET	998.09	88 057	–0.192	99.63	99.82

According to Guideline DKD-R 8-1 [4], the "*process-related handling contribution*" is a minimum value which cannot be omitted when estimating the measurement uncertainty; this contribution value encompasses the influences on the dispensed volume which occur due to the handling of the devices during the calibration of piston-operated pipettes. The DKD-R 8-1 guideline recommends taking it into account in the uncertainty budget with at least 0.07 % of the nominal volume for single-channel piston-operated pipettes with a fixed volume. This contribution was added to the uncertainty budget of the laboratories in order to have a more realistic uncertainty result. The final results for piston pipettes with all corrections applied for volume and uncertainty are presented in Table 12.

The uncertainty values reported by CENAM in Table 6 already include the "process-related handling contribution”. Therefore, these uncertainties values remain without change in Table 12.

Table 12. Corrected volume measurement results with associated uncertainty

100 µL TS	**Piston pipette 153603A**				**Piston pipette 153607A**			
	Calibration 1		Calibration 2		Calibration 1		Calibration 2	
	V/µL	*U*/µL	*V*/µL	*U*/µL	*V*/µL	*U*/µL	*V*/µL	*U*/µL
CENAM	100.01	0.20	99.98	0.20	99.88	0.20	99.90	0.20
IBMETRO	99.88	0.15	99.79	0.15	99.87	0.14	99.69	0.14
LATU	100.15	0.58	100.06	0.48	100.11	0.49	99.88	0.35
INTN	100.10	0.24	100.10	0.24	100.00	0.20	99.90	0.20
INEN	99.39	0.33	--	---	99.18	0.27	--	---
INDECOPI	100.15	0.20	100.08	0.18	100.03	0.17	100.05	0.18
INM	100.21	0.21	99.81	0.22	99.56	0.18	99.49	0.16
LACOMET	99.98	0.54	99.96	0.58	99.68	0.65	99.82	0.51

	CRV/µL	*U*(*CRV*)/µL	*CRV*/µL	*U*(*CRV*)/µL
CRV	99.985	0.084	99.897	0.084
Method	Weighted mean		Weighted mean	

The comparison reference value *CRV* was calculated for each piston pipette using the mean of the calibration 1 and calibration 2 of the final results with all corrections applied for volume and uncertainty.

6. DETERMINATION OF THE CONSISTENCY

The *CRV* for each transfer standard was determined according to the procedures suggested by Cox [5], calculating the weighted mean and its uncertainty.

To identify inconsistent results, a chi-square test is applied to the calibration results [5]:

$$\chi^2_{\text{obs}} = \frac{(x_1 - y)^2}{u^2(x_1)} + \ldots + \frac{(x_n - y)^2}{u^2(x_n)} \tag{3}$$

where the degree of freedom is expressed by $\nu = n - 1$.

The consistency check is regarded as failed, if the probability $\Pr\{\chi^2(\nu) > \chi^2_{\text{obs}}\} < 0.05$.

6.1 Pycnometers

When calculating the *CRV* for the pycnometer 11.04.08 by the Cox method, the chi-square test for $\nu = 7$ gives $\chi^2(\nu) = 14.07 > \chi^2_{\text{obs}} = 13.66$. Therefore, the results are consistent with each other and with the reference value from a statistical point of view. The measurement results for this pycnometer, the reference value and its uncertainty are presented in Figure 3.

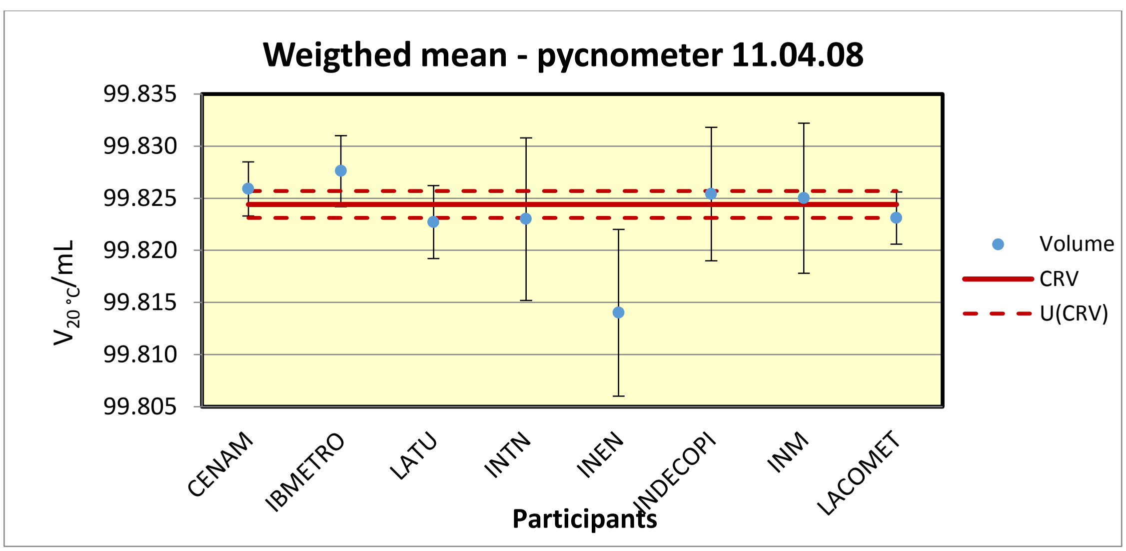

Figure 3. Measurement results of the pycnometer 11.04.08. The distance between two red lines expresses the expanded uncertainty of the reference value, with $k = 2$.

When calculating the *CRV* for the pycnometer 11.04.09 by the Cox method, the chi-square test for $\nu = 7$ gives $\chi^2(\nu) = 14.07 < \chi^2_{\text{obs}} = 24.60$. Therefore, the results are not consistent with each other and with the reference value from a statistical point of view.

If the result of INM is removed from the subset because it is the most discrepant value, and a new calculation of the *CRV* is performed according to the Cox procedure, we obtain $\nu = 6$, $\chi^2(\nu) = 12.59 > \chi^2_{obs} = 9.36$. The consistency check passes, i.e. the remaining values are consistent with each other and with the new reference value of 100.513 3 mL and its expanded uncertainty of 0.001 3 mL. The measurement results for this pycnometer, the reference value and its uncertainty are presented in Figure 4.

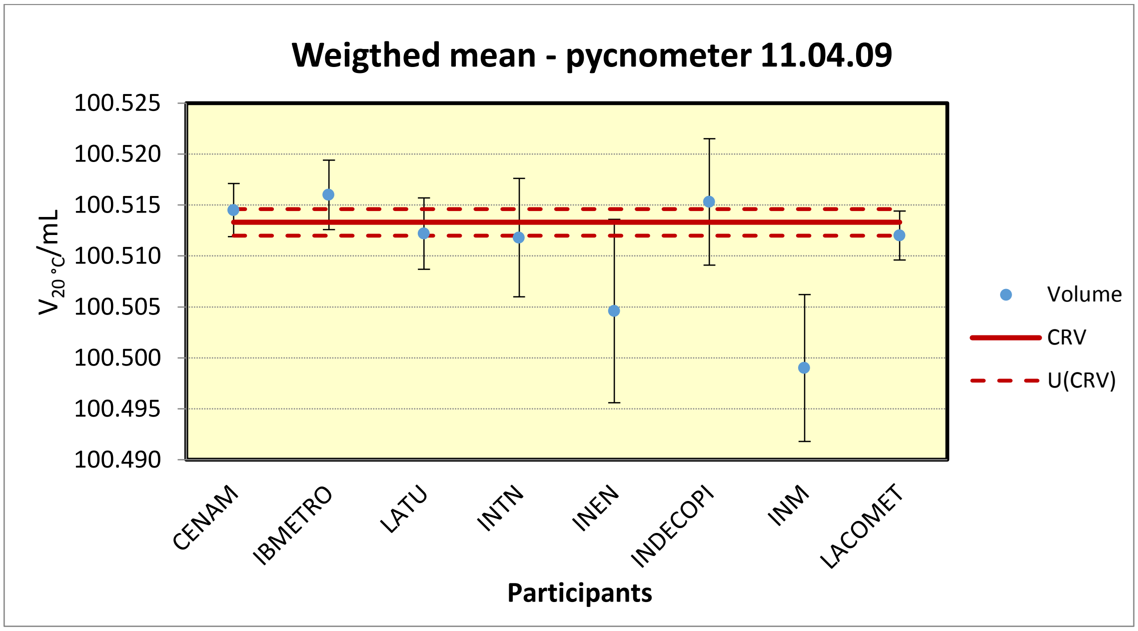

Figure 4. Measurement results of the pycnometer 11.04.09 with uncertainties expressed at k = 2. The distance between two red lines expresses the expanded uncertainty of the reference value.

6.2 Piston Pipettes

When calculating the *CRV* for the piston pipette 153603A by the Cox method, the chi-square test for $\nu = 7$ gives $\chi^2(\nu) = 14.07 < \chi^2_{obs} = 19.20$. Therefore, the results are not consistent with each other and with the reference value from a statistical point of view.

If the result of INEN is removed from the subset because it is the most discrepant value, and a new calculation of the *CRV* is performed according to the Cox procedure, we obtain $\nu = 6$, $\chi^2(\nu) = 12.59 > \chi^2_{obs} = 7.05$. The consistency check pass, i.e. the remaining values are consistent with each other and with the new reference value of 99.985 µL and its expanded uncertainty of 0.084 µL. The measurement results for the piston pipette 153603A, the reference value and its uncertainty are presented in Figure 5.

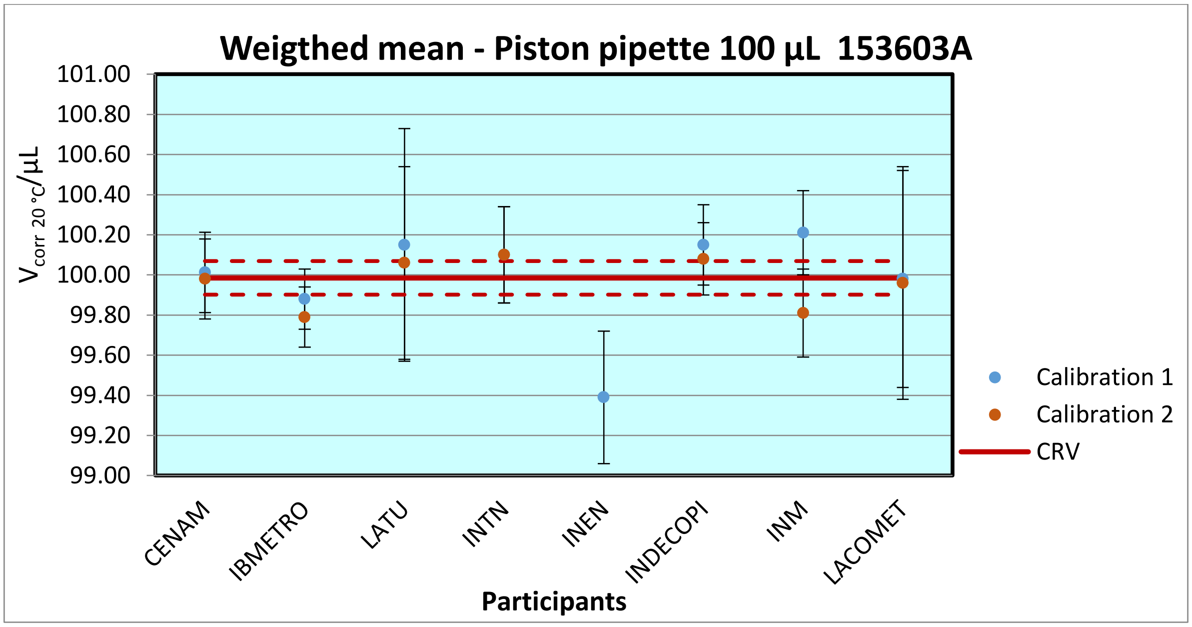

Figure 5. Measurement results of the piston pipette 153603A. The distance between two red lines expresses the expanded uncertainty of the reference value

In the case of the calculation of the *CRV* for the piston pipette 153607A by the Cox method, the chi-square test for $\nu = 7$ gives $\chi^2(\nu) = 14.07 < \chi^2_{obs} = 42.74$. Therefore, the results are not consistent with each other and with the reference value from a statistical point of view.

If the result of INEN is removed from the subset because it is the most discrepant value, and a new calculation of the *CRV* is performed according to the Cox procedure, we obtain $\nu = 6$, $\chi^2(\nu) = 12.59 < \chi^2_{obs} = 21.61$, i.e. the consistency check fails again. The procedure is now repeated removing the result from INM (the most discrepant value) from the subset and a new calculation of the *CRV* is performed. The consistency check finally passes with $\nu = 5$, $\chi^2(\nu) = 11.07 > \chi^2_{obs} = 6.23$, i.e. the remaining values are consistent with each other and with the new reference value of 99.897 µL and its expanded uncertainty of 0.084 µL. The measurement results for the piston pipette 153607A, the reference value and its uncertainty are presented in Figure 6.

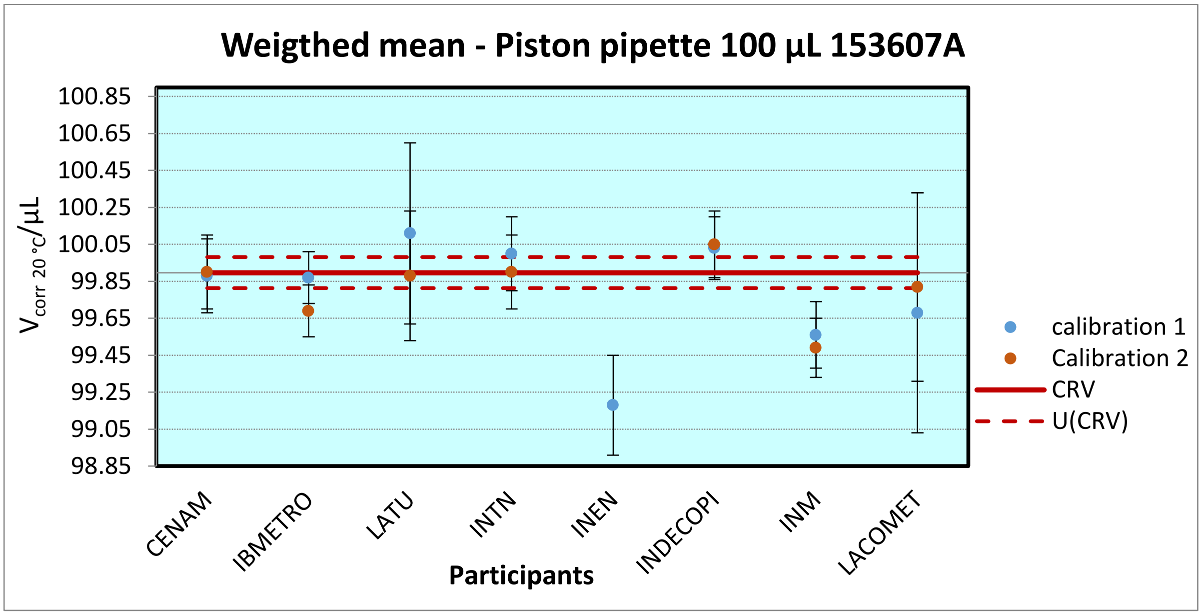

Figure 6. Measurement results of the piston pipette 153607A with uncertainties expressed at k = 2. The distance between two red lines expresses the expanded uncertainty of the reference value.

Before submission of this Draft A report, two participants were asked to verify their submitted results: The INEN and the INM have been informed that their results appeared to be discrepant based on the obvious identifying of discrepancy in Procedure A of Cox [5]. Attempts were made to resolve the inconsistency; however, after reviewing the calculations, just negligible differences were found by the laboratories.

7. DEGREES OF EQUIVALENCE

7.1 Degree of equivalence d_i related to *CRV*

The degree of equivalence d_i of each result of the participating NMIs is expressed quantitatively as the deviation from the comparison reference value *CRV*, and the uncertainty of this deviation is given at the 95 % level of confidence.

To calculate the degrees of equivalence d_i between the *CRV* and the corresponding NMIs, the following formulas are applied [5].

$$d_i = x_i - x_{\mathrm{ref}} \tag{4}$$

$$U(d_i) = 2 \times u(d_i) \tag{5}$$

where $u(d_i)$ is given by

$$u^2(d_i) = u^2(x_i) - u^2(x_{\mathrm{ref}}) \tag{6}$$

Discrepant values can be identified, if $| d_i | > 2u\,(d_i)$.

The normalized error $E_{\mathrm{N},i}$ describes the degree of equivalence of a laboratory related to the *CRV*. $E_{\mathrm{N},i}$ was calculated for each reported value of participants as follows,

$$E_{\mathrm{N},i} = d_i/U(d_i) \tag{7}$$

If $| E_{\mathrm{N},i} | \leq 1$, the measurement is generally considered as acceptable and the measured values are consistent.

Figures 7 and 8 show the degree of equivalence (d_i) of the artifacts calculated with the respective reference value of the transfer standards. Uncertainty bars are expressed with a coverage factor of $k = 2$.

The degree of equivalence d_i and the normalized error $| E_{\mathrm{N},i} |$, for the 100 mL pycnometers and for the 100 µL piston pipettes, are shown in Table 13 and Table 14, respectively.

Table 13. Degree of equivalence d_i and normalized error $E_{N,i}$ for the 100 mL pycnometers

NMI	Pycnometer 11.04.08			Pycnometer 11.04.09		
	d_i/mL	$U(d_i)$/mL	$\|E_{N,i}\|$	d_i/mL	$U(d_i)$/mL	$\|E_{N,i}\|$
	$\times 10^{-3}$		$d_i/U(d_i)$	$\times 10^{-3}$		$d_i/U(d_i)$
CENAM	1.5	2.3	0.67	1.2	2.3	0.53
IBMETRO	3.2	3.1	1.0	2.7	3.1	0.86
LATU	–1.7	3.2	0.52	–1.1	3.2	0.34
INTN	–1.4	7.7	0.18	–1.5	5.7	0.27
INEN	–10.4	7.9	1.3	–8.7	8.9	0.98
INDECOPI	1.0	6.3	0.16	2.0	6.1	0.33
INM	0.6	7.1	0.08	–14.3	7.1	2.0
LACOMET	–1.3	2.1	0.61	–1.3	2.0	0.64

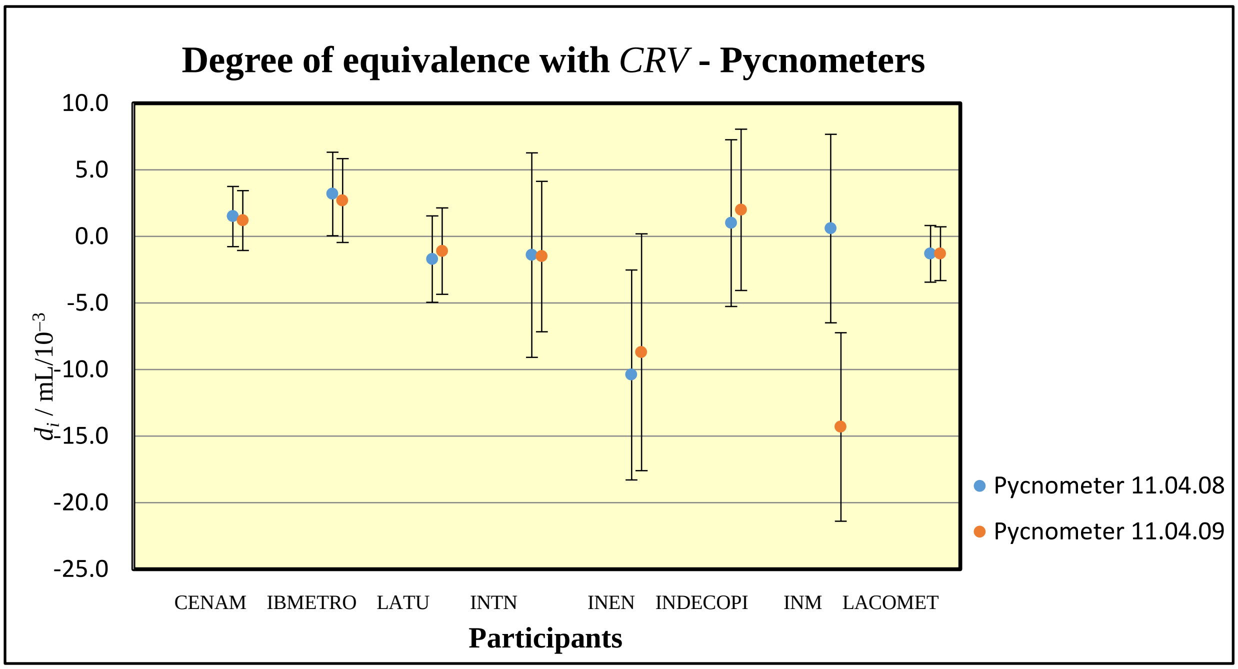

Figure 7. Degree of equivalence of each laboratory with respect to the reference value for the measurements of the pycnometers

Table 14. Degree of equivalence d_i and normalized error $E_{N,i}$ for the 100 µL piston pipettes

100 µL TS	Piston pipette 153603A						Piston pipette 153607A					
	Calibration 1			Calibration 2			Calibration 1			Calibration 2		
	d_i/µL	$U(d_i)$/µL	$\|E_{N,i}\|$	d_i/µL	$U(d_i)$/µL	$\|E_{N,i}\|$	d_i/µL	$U(d_i)$/µL	$\|E_{N,i}\|$	d_i/µL	$U(d_i)$/µL	$\|E_{N,i}\|$
	$\times 10^{-2}$		$d_i/U(d_i)$	$\times 10^{-2}$		$d_i/U(d_i)$	$\times 10^{-2}$		$d_i/U(d_i)$	$\times 10^{-2}$		$d_i/U(d_i\|$
CENAM	2.5	18	0.14	-0.50	18	0.03	– 1.7	18	0.094	0.30	18	0.017
IBMETRO	–11	12	0.84	-19	12	1.6	– 2.7	11	0.24	–21	11	1.8
LATU	17	57	0.29	8.0	47	0.16	21	48	0.44	– 1.7	34	0.050
INTN	11	22	0.51	11	22	0.51	10	18	0.57	0.30	18	0.017
INEN	–59	32	1.9	--	--	--	–72	26	2.8	--	--	--
INDECOPI	17	18	0.91	9.5	16	0.60	13	15	0.90	15	16	0.96
INM	22	19	1.2	–17	20	0.86	–34	16	2.1	–41	14	3.0
LACOMET	-0.50	53	0.009	–2.5	57	0.044	–22	64	0.34	– 7.7	50	0.15

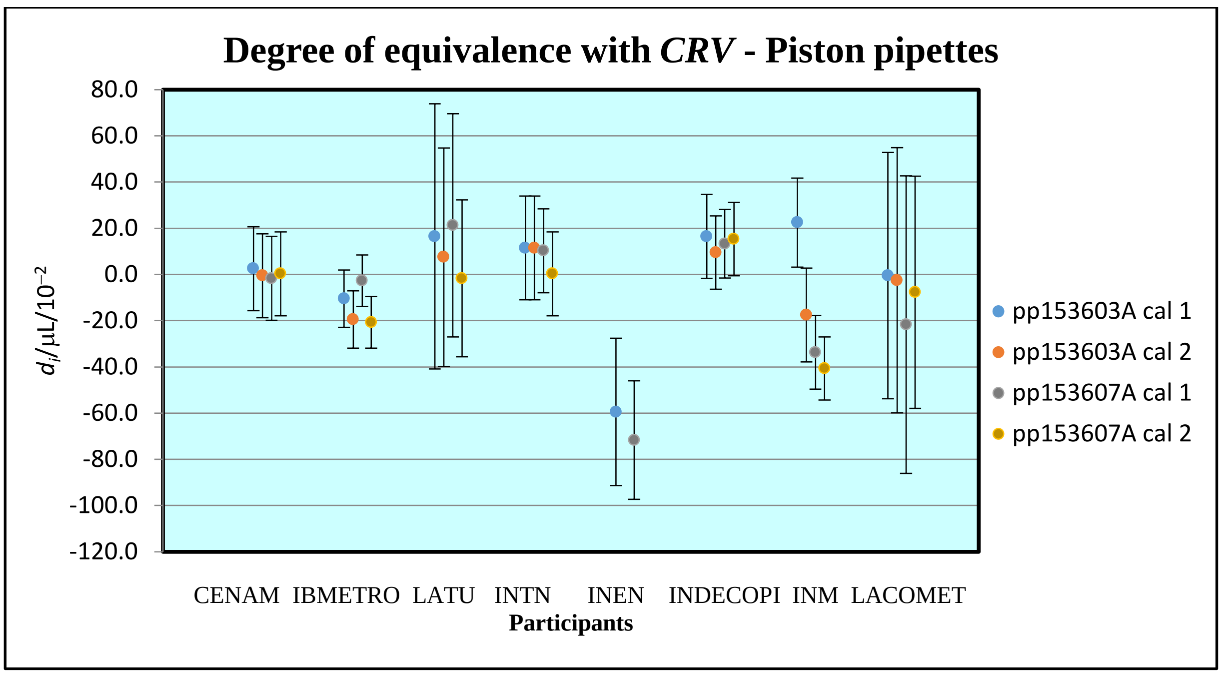

Figure 8. Degree of equivalence d_i with the *CRV* and uncertainty for the measurement of the piston pipettes

8. CONCLUSIONS

The main objective of the comparison was to compare the performance of volume of liquid measurements of the participating laboratories from ANDIMET, as well as from other SIM laboratories, using two100 mL pycnometers and two 100 µL piston pipettes.

The selected transfer standards showed a stable volume during the whole comparison period. This stability was verified by CENAM.

As can be seen in Figures 3 and 4, most of the 100 mL pycnometer results are consistent and overlap with the *CRV*, except the INEN result for the pycnometer 11.04.08 and the INM result for the pycnometer 11.04.09. These two results, with normalized errors $|E_{N,i}|$ of 1.3 and 2.0, respectively, are considered discrepant. The degrees of equivalence of 6 from 8 NMIs agree within ± 0.003 %.

In the case of the 100 µL piston pipettes, the reported results by the NMIs participants were corrected by the influence of the altitude from the place of the calibration. Besides, the uncertainty contribution due to the "process-related handling contribution" was added in the uncertainty budget with a value of 0.07 % of the nominal volume, as recommended by the Guideline DKD-R 8-1.

The corrected results of most laboratories are consistent and overlap with the *CRV* for both calibrations of each piston pipette. The results from INEN and some from INM and IBMETRO are regarded as discrepant, as their normalized errors $|E_{N,i}|$ are greater than 1. The best estimation of the measured value, as reported by the participants, shows a good agreement in 7 of 8 NMIs of better than ± 0.3 %.

9. REFERENCES

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ANNEX A. EQUIPMENT DESCRIPTION AND TRACEABILITY

Table A.1. Balance - Pycnometers 100 mL

NMI	Manufacturer	Model	Upper range value/g	Resolution/ mg	Standard uncertainty/ mg	Calibration date	Traceability
CENAM	Mettler Toledo	AT400	405	0.1	0.15	2011-03-25	CENAM
IBMETRO	Sartorius	BP220S	220	0.1	0.4	2012-02	LATU
LATU	Mettler Toledo	AG 204	200	0.1	$U_{exp}/g = Uo + B \cdot L + Cc \cdot L$ Uo = 0.000 61 g $B = 1.82E^{-6}$ $Cc = 1.00E^{-6}$ L = Balance reading	2011-12-13	BIPM
INTN	Sartorius	ME 235 S	230	0.01	0.225	2012-05-10	ONM
INEN	Mettler Toledo	XP 504	520	0.1	0.2	2012-01-10	INEN-CENAM
INDECOPI	OHAUS	DV215CD	210	0.1	0.17	2012-08-15	INDECOPI
INM	Mettler Toledo	XP 205	200	0.01	0.02	2013-05-07	INM
LACOMET	Mettler Toledo	AT 201	200	0.1	0.4	2012-08	LACOMET

Table A.2. Balance – Piston pipettes 100 µL

NMI	Manufacturer	Model	Upper range value/g	Resolution/ mg	Standard uncertainty/ mg	Calibration date	Traceability
CENAM	Mettler Toledo	XP205	220	0.01	0.04	2012-12	CENAM
IBMETRO	Mettler Toledo	AT1005	100	0.01	0.4	2012-02	LATU
LATU	Shimadzu	AUW 120D	40	0.01	U_{exp}/g = $Uo + B \cdot L + Cc \cdot L$ Uo = 0.000 61 g $B = 1.82E^{-6}$ $Cc = 1.00E^{-6}$ L = Balance reading	2012-05-18	BIPM
INTN	Sartorius	ME 235 S	230	0.01	0.225	2012-05-10	ONM
INEN	Mettler Toledo	XP205	220	0.01	0.01	2012-01-10	INEN-CENAM
INDECOPI	Ohaus Mettler	DV215CD ---	80 5	0.01 0.001	0.024 0.005	2012-08-15 2012-07-17	INDECOPI INDECOPI
INM	Mettler Toledo	XP 205	200	0.01	0.02	2013-05-07	INM
LACOMET	Mettler Toledo	AT 201	60	0.01 g	0.14	2012-08	LACOMET

Table A.3. Weights

NMI	Manufacturer	Model	Range/g	Calibration date	Traceability
CENAM	Rice Lake	E2	0.001 to 1 000	2012	CENAM
IBMETRO	Sartorius	---	100	2009	LATU
LATU	---	---	---	---	---
INTN	Murakami Koki CO LTD.	Cylindrical	0.001 to 2 000	2011-04-29	ONM
INEN	Mettler Toledo	---	500 to 200	2012-05-08	INEN-CENAM
INDECOPI	Kern & Sohn GmbH	---	1 to 100	---	INDECOPI
INM	Häfner	Wire / Cylindrical	200	2012-10-12	INM
LACOMET	Sartorius Mettler Toledo	F1 E2	0.001 to 1 000 0.001 to 200	2013 2010	LACOMET LACOMET

Table A.4. Water thermometer

NMI	Manufacturer	Model	Range/ ºC	Resolution/ ºC	Standard uncertainty/ ºC	Calibration date	Traceability
CENAM	ERTCO	63C	0 to21	0.01	0.02	2009-05-27	CENAM
IBMETRO	Oakton	TEMP14	100	0.1	0.1	2006	PTB
LATU	Tinsley Newport	5187SA True RMS	–180 to 660 0 to 40	0.00001 0.1	0.010 0.35	2008-10-06 2012-05-22	PTB PTB
INTN	Extech	407907		0.1	0.05	2012-02-17	ONM
INEN	Ahlborn Fluke	2490 52II	–200 to 850 –200 to 1370	0.01 0.1	0.04 0.1	2012-04-18 2012-04-18	INEN-CENAM INEN-CENAM
INDECOPI	Hanna Instruments	Checktemp1	–50 to 150	0.1	0.05	2012-08-16	INDECOPI
INM	Thermoschneider	772204	40	0.05	0.03	2012-06-08	INM
LACOMET	Ahlborn	PT 100 ALMEMO MA 2490	N.A.	0.01	0.02	2012-03	LACOMET

Table A.5. Air thermometer

NMI	Manufacturer	Model	Range/ ºC	Resolution/ ºC	Standard uncertainty/ºC	Calibration date	Traceability
CENAM	Vaisala	HM34C	N.A.	0.1	0.1	2013-03-08	CENAM
IBMETRO	Testo	177-H1	100	0.1	0.1	2006	PTB
LATU	No brand	-	0 a 50	0.1	0.50	2011-03-10	PTB
INTN	PCE	PCE 313 - A	60	0.1	0.15	2012-04-05	ONM
INEN	Extech	RH520	–17 to 50	0.1	0.1	2012-04-13	INEN-CENAM
INDECOPI	Luft	OPUS	–20 to 50	0.1	0.35	2012-09-06	INDECOPI
INM	Thermoschneider	816764	30	0.05	0.013	2012-03-30	INM
LACOMET	Vaisala	PTU 200	N.A.	0.1	0.2	2012-10	LACOMET

Table A.6. Barometer

NMI	Manufacturer	Model	Range / hPa	Resolution/ hPa	Standard uncertainty/ hPa	Calibration date	Traceability
CENAM	Druck	DPI 740	600 to 1000	0.01	0.04	2013-05-24	CENAM
IBMETRO	Luft	OPUS II	1300 hPa	0.1	0.1	2008	DKD
LATU	Druck	DPI 740	750 to 1150	0.01	0.14	2007-12-14	INTI
INTN	PCE Group	PC-APM30	300 to 1 200	0.1	0.25	2011-02-10	INTI
INEN	Druck	DPI 740	34 to 1355	0.01	0.031	2012-02-24	INEN-NIST
INDECOPI	Richard-Pekly	NG 5494	960 mbar to 1 060 mbar	1 mbar	0.3 mbar	2012-09-12	INDECOPI
INM	Opus 20	8120.11	1 000 mbar	0,1 mbar	0.15 mbar	2013-01-30	INM-PTB
LACOMET	Vaisala	PTU 200	N.A.	0.1	0.1	2012-09	LACOMET

Table A.7. Hygrometer

NMI	Manufacturer	Model	Range/ % HR	Resolution/ %	Standard uncertainty/ %	Calibration date	Traceability
CENAM	Vaisala	HM34C	100	0.1	0.3	2013-03-08	CENAM
IBMETRO	Testo	177-H1	100	0.1	0.1	2006	PTB
LATU	No brand	-	30 to 80	1	3.5	2011-03-10	PTB
INTN	PCE	PCE 313 - A	100	0.10	0.40	2012-04-05	ONM
INEN	Extech	RH520	10 to 95	1	1.6	2012-04-13	INEN-CENAM
INDECOPI	Luft	OPUS	10 to 95	0.1	1.8	2012-09-06	INDECOPI
INM	Haenni	20761	100	1	1.4	2012-04-12	INM
LACOMET	Vaisala	PTU 200	N.A.	1	2	2012-10	LACOMET