Proyecto PTB CAN Project

ANDIMET plus

SUPPLEMENTARY COMPARISON BETWEEN REGIONAL METROLOGY NATIONAL INSTITUTES OF THE ANDEAN REGION FOR VOLUME 100 mL and 100 µL

Comparison of volumes of 100 mL - calibration of pycnometers

Comparison of volumes of 100 µL - piston pipette calibration

Technical Protocol

Coordination: María del Carmen Vega Amonzabel

IBMETRO Laboratorio de Volumen

March 16, 2012

CONTENTS

1. Introduction.

During the coordination meeting ANDIMET held within the framework CAN-PTB in La Paz, Bolivia, on 31 May and 1 June 2011, it was agreed to conduct a series of comparisons between the National Metrological Institutes (IMNs) of Andean Region which includes a comparison in the magnitude of volume. This comparison has as main purpose to compare the performance of volume measurements using 2 pycnometers of 100 mL and 2 piston cylinders 100 μL, that allows participating laboratories ANDIMET plus provide evidence to support their measurement and calibration capabilities (CMCs) and link the results of this comparison to the corresponding key comparison.

This protocol describes the volumetric devices involved in the comparison, the methods and equations used for the determination of its volume, the experimental conditions and the way the results of measurements should be reported with associated uncertainties.

The organization of the comparison will be coordinated by the Laboratory of Volume of the Bolivian Institute of Metrology - IBMETRO, with the technical assistance of Sonia Trujillo and Manuel Maldonado from CENAM.

In this comparison, the CENAM serve as the reference laboratory, carrying out measurements pycnometers and piston cylinders at the beginning and end of the round of measurements between different participating NMIs.

2. Organization.

The organization of comparison will be coordinated by the Bolivian Institute of Metrology as pilot laboratory, specifically by Mrs. Maria del Carmen Vega from Laboratory of Volume

2.1 Participants.

La siguiente tabla muestra los laboratorios participantes de esta comparación:

Contact	NMI	Information
Abed Morales	**INDECOPI – PERU**	**amorales@indecopi.gob.pe**
Manuel Salazar	**INEN- ECUADOR**	**msalazar@inen.gob.ec**
Pablo Solano	**SIC- COLOMBIA**	**psolano@correo.sic.gov.co**

Maria Vega	**IBMETRO-BOLIVIA**	**mvega@ibmetro.gob.bo**
Andrea Sica	**LATU- URUGUAY**	**Asica@latu.org.uy**
Diana Cantero	**INTN- PARAGUAY**	**dcantero@intn.gov.py**
Sonia Trujillo	**CENAM-MEXICO**	strujill@cenam.mx

Table1.- Participants Laboratories

2.2 Dates for measurement.

Equipments will be circulated in accordance with the timetable set out in Table 2.

Laboratory	***Country***	***Date***
CENAM	Mexico	2012-01-15
1 IBMETRO	Bolivia	2012-03-19
2 LATU	Uruguay	2012-04-23
3 INTN	Paraguay	2012-05-28
4 INEN	Quito Ecuador	2012-07-02
5 INDECOPI	Peru	2012-08-06
6 INM	Colombia Bogotá	2012-09-10
7 LACOMET	Costa Rica	2012-10-15
CENAM	Mexico	2012-11-19

Table 2.- Dates of the comparison.

By accepting these guidelines, participating laboratories are committed to the care of the patterns and delivery on time the next lab.

2.3 Transport and costs

Transport to the next laboratory, according to the program of section 2.2 of this document is the responsibility of each participant to deliver on the agreed date, will take out the gear. Transport costs are covered by financial support from the PTB project "Promoting coordinated quality infrastructure in the Andean Region", except Uruguay, Paraguay and Costa Rica that the costs are assumed by each National Metrology Institute.

After completing the measurements, the participating laboratory must take the pattern to the next reported laboratory according to protocol. It is recommended that laboratory personnel designated for transport and delivery patterns attends for possible inquiries inspection officials during the trip.

2.4 Receipt of patterns

Immediately after the arrival of the patterns, the elements must be unpacked by an expert in volume calibration and should be visually inspected together with the laboratory personnel performing the delivery for damage. The results of this inspection shall be recorded in the "Report form Receipt" attached in Appendix A of this document. The volume laboratory of IBMETRO as pilot laboratory for this comparison, must be informed of the dates of receipt and delivery patterns and the results of visual inspection as soon as possible, sending the format of receipt by mail address.

2.5 Handling and Storage

The handling and storage of patterns in the laboratory is the same laboratory procedure used for similar materials, taking into account the importance of this to the completion of this comparison.

In case of failure of any of the devices shipped, or pycnometer piston pipette, the pilot laboratory must be informed of this situation as soon as possible.

During transportation or the measurement the NMI in charge must bear the cost the equipment replacement.

3. Description of the Patterns.

To make this comparison we have selected 2-Glass pycnometers Gay-Lussac 100 mL and 2-piston pipettes with fixed volume of 100 µL nominal volume. To aspirate the liquid piston, pipettes need to be attached to a removable plastic tip, the tip should be replaced for each measurement. The piston pipettes with the tips are given in appropriate and sufficient quantity to carry out this test. The characteristics of the equipment are described in Table 3.

Quantity	Volume	Material	Mark
2	Pycnometers 100 mL	Glass	Brand
2	Piston pipette fix volume 100 µL	Polypropylen and Fortron	Eppendorf

Tabla 3. Instruments

4. Measurement instructions.

Pycnometers, piston pipettes and tips, should not be touched with bare hands. Should be stored in a place where they are protected from dust, aerosols and vapors as long as no measurements are being made.

Each participating laboratory must use their own instruments and procedures.

The measurement of the patterns are made according to routine laboratory procedure, however, participants must follow the following instructions:

a) The pycnometers and piston pipettes should be calibrated by the gravimetric method.

b) Undertake 10 measurements for each calibration. For the case of the piston pipette two events will be reported by instrument

c) It is recommended to use the Tanaka equation to determine the density of water [1].

The results should include:

- Environmental conditions,
- The volume value referenced at 20 ° C,
- Uncertainty at 95.45% confidence and the value of k,
- "Results Sheet" (see attachment) described in this document.

4.1 Measuring pycnometers.

According to the manufacturer of pycnometers, the cubic coefficient of thermal expansion is (9.9 ± 1) · 10-6 ° C-1 (The uncertainty is expressed as standard uncertainty).

4.2 Measurement of Piston Pipettes

The piston pipettes used in this comparison will use a cubic coefficient of thermal expansion of (2.4 ± 0.24) · 10-4 ° C-1 [2]

The calibrations of the pipette piston consist in determining the amount of water delivered to the pipette 20 ° C using the gravimetric method.

Important considerations in accordance with ISO 8655 [3] to be taken into account in order to avoid measurement errors:

- The weighing container should have a small amount of water to reach a minimum height of 3 mm from the vessel before starting the measurements. It is recommended to use a container with lid or trap evaporation. The heavy weight of container including water and cover if any is the tare weighted before the first measurement.
- The water delivered to the pipette weighing vessel is performed by supporting the pipette tip into the container wall at an angle of 30 ° to 45 ° from the vertical. After flushing, the pipette tip trailing (8-10) mm along the vessel wall.
- To initiate each calibration event should be saturated the pipette piston with moisture charging and discharging water, 5 times with the same tip.
- Change the tip and moisten before each measurement.
- Each participating laboratory must make 10 consecutive measurements for each calibration event.

4.3 Uncertainty of measurement.

Each of the participating laboratories must send together with the results, the evaluation of measurement uncertainty according to the ISO Guide for the Expression of Uncertainty in Measurement [4] considering the exceptions set out in this protocol.

The mathematical model for determining the volume and measurement uncertainties, were made according to ISO 4787 [5] as follows:

$$V_{20} = m_w \cdot \left(\frac{1}{\rho_w - \rho_A} \right) \cdot \left(1 - \frac{\rho_A}{\rho_B} \right) \cdot \left(1 - \alpha \left(t_d - 20 \right) \right)$$

where:

$V_{20} / \mathrm{mL}, \mu\mathrm{L} =$ Volume at 20 °C by the calibrated vessel

m_w /g,mg = Mass of water contained or supplied by the calibrated vessel

$\rho_\omega / \mathrm{g/cm^3} =$ Density of water at the calibration temperature

ρ_A /g/cm^3 = Air density at the calibration conditions

ρ_B /g/cm^3 = Density of the weights with which the balance was calibrated

α /°C^{-1} = Cubic coefficient of thermal expansion of the container material wich is calibrated

t_d °C = Temperature of the container taken in °C

For consideration of the estimated uncertainty in the model, do not take into account the correlation between variables as agreed in the initial workshop by the participants of the National Metrology Institutes,.

To estimate the standard uncertainty type A piston pipettes have been agreed at the meeting starting, use the standard deviation, i.e. without dividing by the number of repetitions performed.

To estimate the uncertainty inthe mathematical model, corrections will be added as deemed necessary.

It should consider at least the following corrections:
- Due to the resolution of the instruments
- Due to the calibration
- Due to the gradients (temperature, humidity, pressure)
- Due to stability over time
- Because Repeatability
- Due to the mathematical models (density of water and air density)
- Because the coefficients of thermal expansion.

5. Reporting of results.

The format of Appendix B.2 shall indicate the technical characteristics of the instrument used and the standard used.

Will report two events of 10 measurements for each piston pipette, ie two forms were filled in Appendix B.3. and two formats for each appendix B.4 piston pipette.

For reporting results of pycnometers only a reported event instrument, ie a format of Appendix B.3. and format of Appendix B.4 for each pycnometer.

These forms will be sent to IBMETRO duly completed and signed by the head of the measurements.

The IBMETRO send their measurement results to CENAM three weeks after making their measurements.

After collecting the results of the NMIs participants, IBMETRO prepare a preliminary report to be analyzed and discussed by the participants. Data analysis comparing with the reference value and its standard error produced by CENAM, then the all the data will be send to IBMETRO to be introduced in the preliminary report. Subsequently convened a meeting to fine tune the last details and proceed with publication of results in a magazine or international forum.

6. 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, Vol.38, 301-309.

2. ASTM E 542:2000 Standard practice for calibration of laboratory volumetric apparatus.

3. ISO 8655-6: 2002, Piston-operated volumetric apparatus. Part 6: Gravimetric methods for the determination of measurement error

4. BIMP, IEC, IFCC, ISO, IUPAC, IUPAP, OIML; Guide to the expression of uncertainty in measurement (GUM), Geneva, 1995

5. ISO 4787:2010; Laboratory glassware - Volumetric glassware – Methods for use and testing of capacity

6. Protocolo de la comparación SIM 2007 para picnómetros SIM.M.M.FF-K4 Technical Protocol for Volume Intercomparison at 20 L and 100 mL

7. Protocolo de la comparación SIM 2007 Suplementaria SIM.L-S1/2007 “Calibración de Bloques Patrón por Comparación Mecánica”

Apendices A. Report form receipt and send standards.

To: IBMETRO
María del Carmen Vega A.
Av. Camacho Nº 1488
TELÉFONO : 591-2-2372046 2310037
Fax: 591-2-2372046 2310037 int 108
e-mail: mvega@ibmetro.gob.bo

From :(Participant laboratory)

Mark with X the option:

- **Confirm we have received the equipment** (insert date of receipt) **confirm we have received the equipment (insert date of receipt)**

_____
_____
_____

- **We confirm that we have delivered the equipment to** (name of person) **on** (insert date of shipment)

After a visual inspection:

- **Not have significant damage and general condition will be reported in the format of Appendix B along with the measurement results.**

- **Presents severe damage threatening the measurement result**. Please indicate the damage, specifying in detail the same and if possible send pictures of the damage, if necessary, use additional sheets to your report

_____
_____
_____
_____
_____

Date: **Name and signature:** **me and signature:**

_____ _____ _____

Appendices B. Report form result

Pycnometer/ Piston pipette

Institute:_____

B.1.Calibration procedure

Description (short)	

B.2. Technical specifications and traceability

B.2.1 TECHNICAL SPECIFICATIONS AND TRACEABILITY **–Piston pipette**							
Instruments							
	Manufacturer	**Type**	**Maximun range**	**Resolution**	**Standard uncertainty**	**Calibration date**	**Traceability**
BALANCE used for weighing in air							
BALANCE used for weighing full							
Weights							
Thermometer water							
Thermometer Air							
Hygrometer							
Barometer							

	Production method	**slighted (yes or not)**	Formula or table for the density	measured conductivity
Water				

B.2.2 TECHNICAL SPECIFICATIONS AND TRACEABILITY **-Pycnometers**							
Instrument							
	Manufacturer	**Type**	**Maximun range**	**Resolution**	**Standard uncertainty**	**Calibration date**	**Traceability**
BALANCE used for weighing in air							
BALANCE used for weighing full							
Weights							
Thermometer water							
Thermometer Air							
Hygrometer							
Barometer							

B.3. Results of measure

Instrument: **Pycnometer 100 ml** Serial number: Date:

Measurement	m_w/g	t_d/°C	ρ_w/ g/mL	t_A/ºC	p/ Pa	H/%	ρ_A/g/mL	$V_{20ºC}$/mL
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
Average								

Weighing method:

Instrument: **Pycnometer 100 ml**			Serial number			Date:		
Measurement	m_w/g	t_d/°C	ρ_w/ g/mL	t_A/ºC	p/ Pa	H/%	ρ_A/g/mL	$V_{20ºC}$/mL
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
Average								
Weighing method:								

Instrument: **Pistón pipete 100 µL**			Serial number			Date:		
Measurement	m_w/mg	t_d/°C	ρ_w/ mg/µL	t_A/ºC	p/ Pa	H/%	ρ_A/mg/µL	$V_{20ºC}$/µL
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
Average								
Weighing method:								

Equipo: **Piston pipete 100 µL**			Serial number			Date:		
Measurement	m_w/mg	t_d/°C	ρ_w/ mg/µL	t_A/ºC	p/ Pa	H/%	ρ_A/mg/µL	$V_{20ºC}$/µL
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
Average								
Weighing method:								

B.4. Format Estimation of uncertainty of pycnometer / piston pipette

See Excel file format named B.4

Apendice C. Report calibration results

Instrument	Serial Number	Units	Volume at 20°C	Standard Desviation	Expanded uncertainty about 95%	Cover Factor
Pycnometer	**08**	**mL**				
Pycnometer	**09**	**mL**				
Piston pipette	**153603A**	**µL**				
Piston pipette	**153606A**	**µL**				

Apendice D.

List of component sent

Instrument	Quantity	Manufacturer	Serial number	Observations
Pycnometer 1	1	Brand	08	
Pycnometer 2	1		09	
Piston pipette 1	1	Eppendorf	153603 A	
Piston pipette 2	1		153609 A	
Puntas	70	Eppendorf		

The manufacturer's name is given only for calibrating the instrument to any other topic.