International Comparison

International comparison of volume measurement standards at 50 l at the CENAM (Mexico), PTB (Germany), Measurement Canada and NIST (USA)

*J. M. Maldonado, R. Arias, H.-H. Oelze,
V. E. Bean, J. F. Houser, C. Lachance
and C. Jacques*

Abstract. The Centro Nacional de Metrología (CENAM), the Physikalisch-Technische Bundesanstalt (PTB), Measurement Canada (MC), and the National Institute of Standards and Technology (NIST) maintain the national primary standard facilities for the measurement of volume in Mexico, Germany, Canada and the United States, respectively. These laboratories have compared volume measurements at 50 l. The comparison was accomplished by each laboratory calibrating a transfer standard volume that was circulated among the laboratories, with the CENAM acting as pilot laboratory. All the participants used gravimetric methods. The maximum and minimum reported volumes differ by 0.0098 %.

1. Introduction

Comparison of primary standard measurement facilities is an essential activity of national metrology institutes as this is the best way to detect flaws in instruments and/or procedures. Experience has shown that when the results of such comparisons differ by more than expected, given the respective uncertainties, the participants search for and correct problems and their metrology is improved. Since volume measurements are the basis for the transfer of custody of valuable fluids, comparison of primary standards of volume is particularly significant.

The CENAM, PTB, MC and NIST maintain the national primary standard facilities for the measurement of volume in Mexico, Germany, Canada and the United States, respectively. These laboratories compared volume measurements at 50 l. The CENAM, acting as the pilot laboratory, provided the transfer standard,
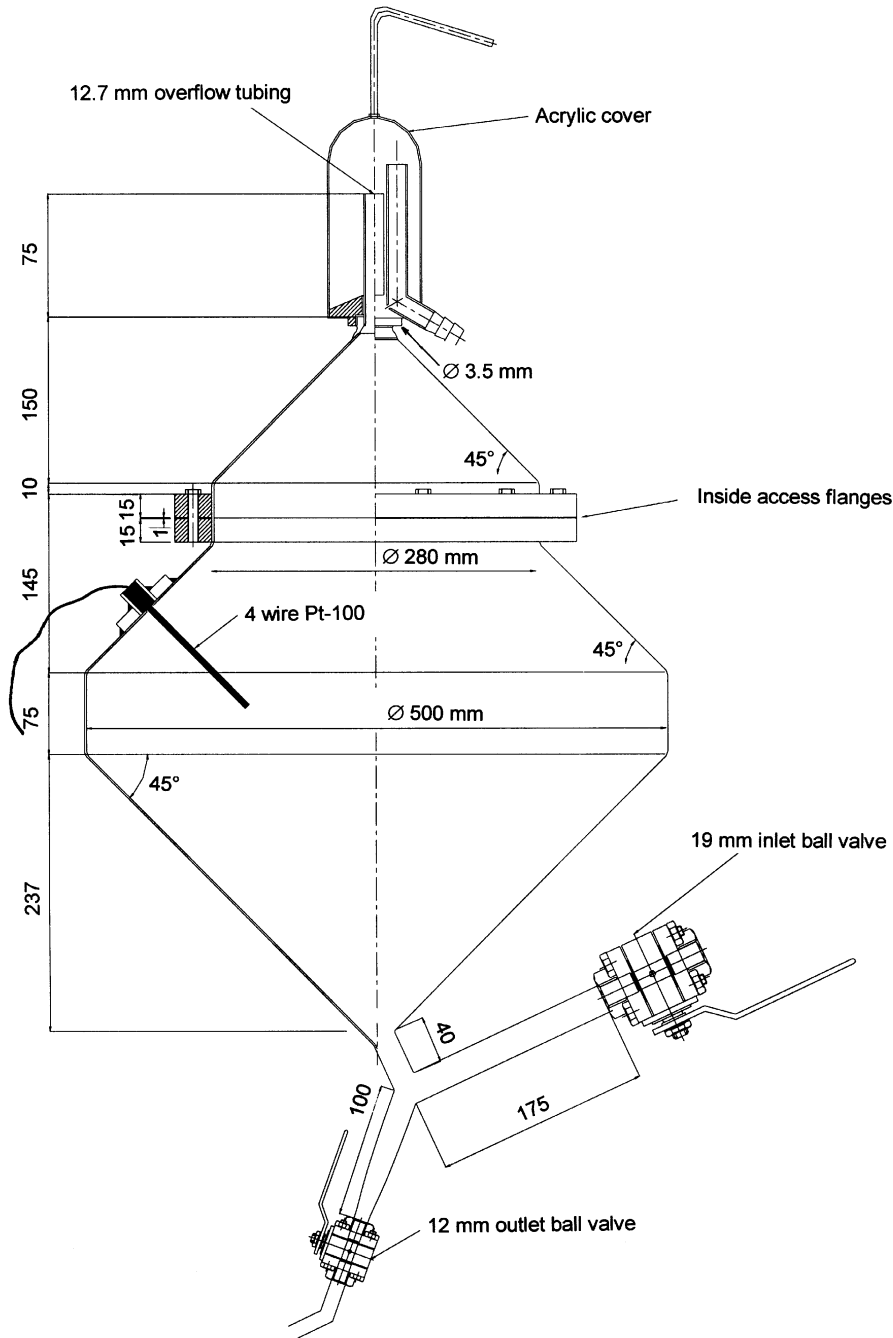
J. M. Maldonado and R. Arias: Centro Nacional de Metrología (CENAM), CP 76900, Querétaro, Mexico.
H.-H. Oelze: Physikalisch-Technische Bundesanstalt (PTB), D-38023 Braunschweig, Germany.
V. E. Bean and J. F. Houser: National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, USA.
C. Lachance: Measurement Canada, Ottawa, K1A 0C9 Ontario, Canada.
C. Jacques: Institute for National Measurement Standards, National Research Council of Canada (NRC), Ottawa, K1A 0R6 Ontario, Canada.

measured the standard before and after shipment to the other laboratories, and organized the comparisons.

2. Transfer standard

The transfer standard, with the exception of the plumbing for filling and draining, was designed by the PTB; the plumbing was designed by the CENAM. The test measure, designed to measure delivered volumes, was made in Mexico from 304-grade stainless steel with welded seams and polished surfaces, inside and out.

Figure 1 is a schematic diagram of the transfer standard. The body is a short, circular cylinder with lobes welded to the sides to allow it to be mounted in a supporting frame. The bottom is closed with a cone welded to the cylinder with the apex downward. The tube welded into the apex branches into the fill line and the drain line, each terminated by a ball valve. The top of the cylinder is similarly closed with a cone. About mid-height, the top cone has a pair of bolted flanges, perpendicular to the cone axis, allowing access to the inside for cleaning. The gasket between the flanges is a negligibly thin coating of silicone grease. A short tube of 8 mm inner diameter is welded into the apex of the top cone. The transfer standard is filled with distilled water until the water protrudes above this tube to the maximum extent permitted by surface tension, thereby defining the filled condition. A transparent acrylic cover

Figure 1. Schematic diagram of the transfer standard. Material 304-grade stainless steel, mirror-quality inner surface, thickness 2 mm, metal-to-metal seal. Dimensions in millimetres.

with an appropriate drain handles any overflow during filling. A thermometer well allows a platinum resistance thermometer to be located near the geometrical centre of the volume.

3. Methods

All the laboratories participating in the comparison used gravimetrically based primary standard facilities for the determination of volume. All used a weigh tank into

which the water in the transfer standard was drained for weighing.

3.1 CENAM and NIST

The CENAM and the NIST used electronic balances with double-substitution weighing designs. Twelve measurements are required for one volume determination using a double-substitution design: eight weighings, plus measurements of water temperature, air temperature, atmospheric pressure and relative

humidity. The steps for the double-substitution technique are [1]:

1. Load calibrated weights, m_e, nominally equivalent to weight of empty weigh tank, on balance and record balance reading as O_{1e}.

2. Remove weights, load empty tank on balance and record reading as O_{2e}.

3. Add sensitivity weight, m_s, say 100 g, to balance and record reading as O_{3e}.

4. Remove tank, reload m_e, add m_s, and record balance reading as O_{4e}.

5. Fill transfer standard with distilled water.

6. Record water temperature, air temperature, barometric pressure and relative humidity.

7. Drain transfer standard into weigh tank and close drain valve 60 s after cessation of main flow. The CENAM, as pilot laboratory, determined the 60 s (drip-off time).

8. Load calibrated weights, m_f, nominally equivalent to weight of weigh tank and 50 l of water, and record reading as O_{1f}.

9. Remove weights, load weigh tank with water on to balance and record reading as O_{2f}.

10. Add m_s and record reading as O_{3f}.

11. Remove weigh tank, reload m_f, add m_s and record reading as O_{4f}.

12. Calculate density of air, ρ_{air}, from measured values of air temperature, atmospheric pressure and relative humidity using an appropriate equation, for example, Davis [2], Giacomo [3], Jaeger and Davis [4], or Jones [5].

13. Calculate A_e, the difference between balance readings of m_e and that of empty weigh tank, via

$$A_e = \frac{O_{2e} + O_{3e} - O_{1e} - O_{4e}}{2} \frac{m_s(1 - \rho_{air}/\rho_s)}{O_{3e} - O_{2e}},$$

where ρ_s is the density of the material from which the sensitivity weight is made.

14. Calculate A_f, the difference between balance readings of m_f and that of weigh tank and distilled water, via

$$A_f = \frac{O_{2f} + O_{3f} - O_{1f} - O_{4f}}{2} \frac{m_s(1 - \rho_{air}/\rho_s)}{O_{3f} - O_{2f}}.$$

15. Calculate density of distilled water, ρ_{water}, from measured water temperature using an appropriate empirical equation, for example, Patterson and Morris [6], Kell [7], Watanabe [8], Takenaka and Masui [9], Wagenbreth and Blanke [10], or Bettin and Spieweck [11].

16. Calculate delivered volume of transfer standard at 20 °C via

$$V = \frac{(m_f - m_e)(1 - \rho_{air}/\rho_{ss}) + A_f - A_e}{\rho_{water} - \rho_{air}} \times$$
$$[1 - \beta(T_{water} - 20)],$$

where β is the volume thermal expansion coefficient of the stainless steel from which the transfer standard is made ($4.77 \times 10^{-5}/°C$), and ρ_{ss} is the density of the material from which the calibrated weights are made.

3.2 MC

The MC used an electronic balance and a single-substitution weighing design without a sensitivity weight. The single-substitution design requires eight measurements for one volume determination: four weighings, plus measurements of water temperature, air temperature, atmospheric pressure and relative humidity. The steps are the same as for the double-substitution design with the omission of steps 3, 4, 10, 11, 13, 14 and 16. The delivered volume at 20 °C is calculated via

$$V = \left(\frac{O_{2f}m_f}{O_{1f}} - \frac{O_{2e}m_e}{O_{1e}}\right) \frac{(1 - \rho_{air}/\rho_{ss})}{\rho_{water} - \rho_{air}} \times$$
$$[1 - \beta(T_{water} - 20)].$$

3.3 PTB

The PTB used an equal-arm balance with a single-substitution weighing design. The steps are:

1. Fill transfer standard with distilled water.

2. Load empty weigh tank and 50 kg of calibrated weights, m_{std}, nominally equivalent to the weight of water in the transfer standard, on one pan of the balance. Load counterweights on the other pan to bring pointer to near mid-scale. Record scale reading as O_1.

3. Unload m_{std}.

4. Record water temperature, air temperature, barometric pressure and relative humidity.

5. Drain transfer standard into weigh tank and close drain valve 60 s after cessation of main flow.

6. Add calibrated weights, Δm_{std}, to pan with weigh tank to bring pointer to near mid-scale. Record scale reading as O_2.

7. Add sensitivity weight, m_s, to balance pan. Record scale reading as O_3.

8. Calculate density of air, ρ_{air}, from measured values of air temperature, atmospheric pressure and

relative humidity using an appropriate equation, for example, Davis [2], Giacomo [3], Jaeger and Davis [4], or Jones [5].

9. Calculate density of distilled water, ρ_{water}, from measured water temperature using an appropriate empirical equation, for example, Patterson and Morris [6], Kell [7], Watanabe [8], Takenaka and Masui [9], Wagenbreth and Blanke [10], or Bettin and Spieweck [11].

10. Calculate delivered volume of transfer standard at 20 °C via

$$V = \left[(m_{\text{std}} - \Delta m_{\text{std}}) \left(1 - \frac{\rho_{\text{air}}}{\rho_{\text{ss}}} \right) - m_{\text{s}} \left(1 - \frac{\rho_{\text{air}}}{\rho_{\text{s}}} \right) \frac{(O_1 - O_2)}{(O_3 - O_2)} \right] \frac{\lfloor 1 - \beta(T_{\text{water}} - 20) \rfloor}{\rho_{\text{water}} - \rho_{\text{air}}}.$$

The transfer standard was disassembled, cleaned and reassembled prior to the series of calibrations conducted by each participant.

4. Results

Table 1 and Figure 2 give in chronological order the volumes and their expanded uncertainties as reported by the laboratories, and the number of measurements, n, that were averaged to obtain each reported volume. The expanded uncertainties, U, were calculated via

$$U = 2\sqrt{u_{\text{A}}^2 + u_{\text{B}}^2},$$

where 2 is the coverage factor and u_{A} is the standard deviation of the average expressed as [12]:

$$u_{\text{A}} = \left[\frac{\Sigma(V_i - \overline{V})^2}{n(n-1)} \right]^{1/2}.$$

The value u_{B} is determined by the characterization of the measurement process by each laboratory. Reproducibility of the transfer standard was not considered for the reported uncertainties.

Table 1. Measured volumes of the transfer standard. The numbers following the symbols ± are the numerical values of the expanded uncertainties ($k = 2$).

Laboratory	Date	Volume/ml	n
CENAM1	October 1997	50 000.6 ± 3.6	9
PTB	November 1997	50 003.8 ± 1.7	8
NIST1	December 1997	50 002.8 ± 0.8	10
CENAM2	March 1998	50 005.5 ± 3.6	22
CENAM3	August 1998	50 001.8 ± 3.7	12
NIST2	September 1998	50 001.7 ± 1.2	11
MC	September 1998	50 000.8 ± 1.2	3
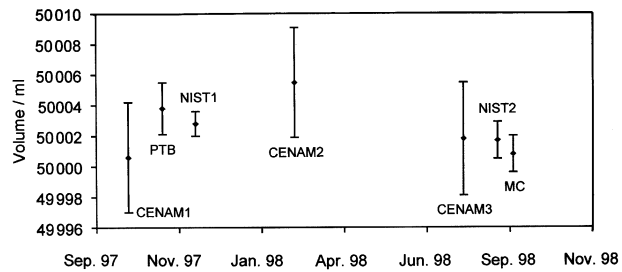
Figure 2. Measured volumes of the transfer standard, in chronological order. The error bars represent the expanded uncertainties ($k = 2$) listed in Table 1.

5. Conclusions

The maximum and minimum reported volumes differ by 0.0098 %. As there are seven sets of measurements, there are twenty-one possible comparisons between pairs of measurements. There is significant overlap of the uncertainties for eighteen of the twenty-one comparisons. The exceptions are PTB/MC, NIST1/MC and CENAM2/MC. The upper limit of the MC error bar is 0.1 ml less than the lower limit of the PTB error bar, indicating no overlap within the expanded uncertainties ($k = 2$) for PTB/MC. The upper limit of the MC error bar is identical to the lower limit of the NIST1 error bar, indicating no overlap within the expanded uncertainties ($k = 2$) for NIST1/MC. The upper limit of the MC error bar is 0.1 ml greater than the lower limit of the CENAM2 error bar, indicating an overlap of only 0.1 ml between the expanded uncertainties ($k = 2$) for CENAM2/MC.

Measurements carried out over short intervals, October 1997 to December 1997 and August 1998 to September 1998, show close agreement and significant overlap of results, with maximum differences of 0.0064 % and 0.002 % respectively.

According to the results, and taking into consideration that the transfer standard was not subject to any thermal stress relaxation process, it is considered that thermal stresses could be a reasonable explanation of the differences among laboratories.

The use of special tools, such as a torque meter, could be of benefit in reducing the variation of the results when using a transfer standard such as that illustrated in Figure 1.

References

1. Houser J. F., *Procedures for the Calibration of Volumetric Test Measures*, Natl. Bur. Stand. (U.S.), NBSIR 73-287, 1973, 22 p.
2. Davis R. S., *Metrologia*, 1992, **29**, 67-70.
3. Giacomo P., *Metrologia*, 1982, **18**, 33-40.
4. Jaeger K. B., Davis R. S., *A Primer for Mass Metrology*, Natl. Bur. Stand. (U.S.), Spec. Publ. 700-1, Industrial Measurement Series, 1984, 79 p.
5. Jones F. E., *J. Res. Natl. Bur. Stand. (U.S.)*, 1978, **83**, 419-428.

6. Patterson J. B., Morris E. C., *Metrologia*, 1994, **31**, 277-288.

7. Kell G. S., *J. Chem. Eng. Data*, 1975, **20**, 97-105.

8. Watanabe H., *Metrologia*, 1991, **28**, 33-43.

9. Takenaka M., Masui R., *Metrologia*, **27**, 1990, 165-171.

10. Wagenbreth H., Blanke W., *PTB-Mitteilungen*, 1971, **81**, 412-415.

11. Bettin H., Spieweck F., *PTB-Mitteilungen*, 1990, **100**, 195-196.

12. *Guide to the Expression of Uncertainty in Measurement*, Geneva, International Organization for Standardization, 1993.