NORAMET Intercomparison of Volume Standards at 50 mL and 100 mL (SIM.M.FF-S1)

C. Jacques
Institute for National Measurement Standards, National Research Council (NRC)
Ottawa, Ontario, Canada K1A 0R6

S. Trujillo Juarez
Centro Nacional de Metrología (CENAM)
Km 4.5 Carr. a los Cués
Mpio. del Marqués, Qro. México

J.M. Maldonado
Centro Nacional de Metrología (CENAM)
Km 4.5 Carr. a los Cués
Mpio. del Marqués, Qro. México

V. Bean
Fluid Flow Group
National Institute of Standards and Technology (NIST)
Gaithersburg, MD 20899, USA

Abstract

An intercomparison of volume standards, 50 mL and 100 mL pycnometers, was decided on at the NORAMET Technical Contacts Meeting of 8-9 June 1998. The participating laboratories were CENAM, NIST, and NRC. NRC acted as the pilot laboratory. The comparison was done between April 1999 and October 1999. The pycnometers were not protected against evaporation by a supplementary cap. Even with this handicap, the three laboratories agreed with one another very well. The difference between maximum and minimum reported volumes never exceeded 0.014 %. This comparison was assigned the number SIM.M.FF-S1.

1. Introduction

An intercomparison of volume standards of 50 mL and 100 mL was decided on at the NORAMET (North American Cooperation in Metrology) Technical Contacts Meeting of 8-9 June 1998. The participating laboratories were Centro Nacional de Metrología (CENAM) of México, National Institute of

Standards and Technology (NIST) of the United States, and National Research Council (NRC) of Canada. NRC was the pilot laboratory.

NRC purchased three sets of Gay-Lussac pycnometers of 50 mL and 100 mL nominal volumes. They were measured first at NRC. Then, two sets were circulated to CENAM and to NIST; the third remained at NRC as a reference. The comparison was done between April 1999 and October 1999.

2. Participants

2.1 CENAM

The liquid density standard used was water grade 1 (ISO 3696); the purification process was filtration, reverse osmosis, de-ionisation, and micro-filtration. The temperature of water was 20 °C with a density of 998.20 $kg \cdot m^{-3}$. The balance used was a commercially available balance, with a resolution of 0.1 mg and a standard uncertainty of 0.2 mg. Two weighing procedures were used: direct reading with ten measurements, and double-substitution with five measurements. The contribution to the uncertainty from these two methods, as well as the reproducibility contribution due to the measurements of three operators, are included in the total uncertainty. The density of air was calculated from measurements of temperature, pressure, and relative humidity.

2.2 NIST

The liquid density standard used was distilled water at a temperature near 23 °C. The balance used was a commercially available balance, with a resolution of 0.01 mg, and a standard deviation of 0.03 mg. Double substitution was used for all the weighings. Air temperature, atmospheric pressure, and relative humidity were measured and the air density was calculated for each weighing. Each pycnometer was weighed ten times when empty and dry. They were also weighed ten times when filled with distilled water. The pycnometers were emptied and refilled with distilled water before each filled weighing. The temperature of the water was measured in the source container before each of the fillings. The density of the water was calculated using the equation of J.B. Patterson and E.C. Morris[1]. The reported values for the temperature and the density of the distilled water and the density of air are averages of ten determinations from measurements and calculations. The reported volumes are referenced to 20 °C.

2.3 NRC

As the pilot laboratory, NRC did the calibration twice, at the beginning of the comparison and at the end. The first time, the liquid density standard used was de-ionised, UV treated double-distilled water. The second time, the water was pre-filtered, single-distilled, de-ionised, ultra-filtered and UV treated water. The density of water from the two processes could not be distinguished; it was calculated from temperature measurements at the end of each measuring sequence, with values around 998.0 kg·m^{-3}. The balance used was a commercially available balance, with a resolution of 0.01 mg and a standard deviation of 0.03 mg. Single substitution was used for all the weighings, with one weighing for the first calibration and six weighings for the last one at the end of the comparison. The density of air was calculated from measurements of temperature, pressure, and relative humidity. The reported volumes are referenced to 20 °C.

3. Data analysis

3.1 Reference value – median

The choice of a reference value is among the mean, the weighted mean, and the median. The median was chosen for its statistical robustness, particularly against the possible outliers. The mean was almost equivalent to the median for this comparison. The weighted mean was not considered because it is less robust than the median.

3.2 Uncertainty of the median

Using the median as the reference value, instead of the mean, is a straightforward process. The method for calculating the uncertainty corresponding to the 1σ level has been addressed by J.W. Müller[2]. The uncertainty to be associated with the sample median $\tilde{m}$ of n observations x_i is

$$s(\tilde{m}) \cong 1.858(n-1)^{-1/2}\,\mathrm{med}\{|x_i - \tilde{m}|\} \quad .$$

3.3 Results and discussion

Figure 1 shows the results of the comparisons by tables and graphs, for each pycnometer: numbers 53 and 365 for 50 mL, and numbers 142 and 322 for 100 mL. The horizontal lines in the graphs delimit the 95 % interval of confidence around the median, the central line. The plotted uncertainties for each point are also the 95 % interval of confidence.

The results of all four sets of calibrations per pycnometer agree in general. There are a few measurements, though, that are worth a comment. For Pyc 53, the 95 % intervals of confidence do not overlap between NIST and NRC-2. NIST is far from the median, at the lower edge of the 95 % of the reference value, but still within the statistical predictions.

An experimental difficulty was the loss of distilled water by wicking between the ground-glass surfaces of the stopper and the neck and subsequent evaporation. NRC measurements show the rate of evaporation to be constant. They took this opportunity to measure the weight of the pycnometer varying with time and report a value at the very time it was filled by extrapolating backward in time (Figure 2). This procedure was used for NRC-2, and gave a lower uncertainty than a single substitution quick measurement at the onset of the evaporation, the latter being used for NRC-1.

4. Conclusion

This comparison between NORAMET countries, Canada, México, and the United States, lasted eight months. The pycnometers were not protected against the evaporation of water by a supplementary cap. Even with this handicap, the three laboratories agreed very well. The difference between maximum and minimum volumes never exceeded 0.014 %. This comparison was assigned the number SIM.M.FF-S1.

5. Acknowledgement

One of the author (CJ) would like to express his gratitude to Dr George Chapman for helping setting up this comparison, and also spending a lot of his precious time in useful discussions.

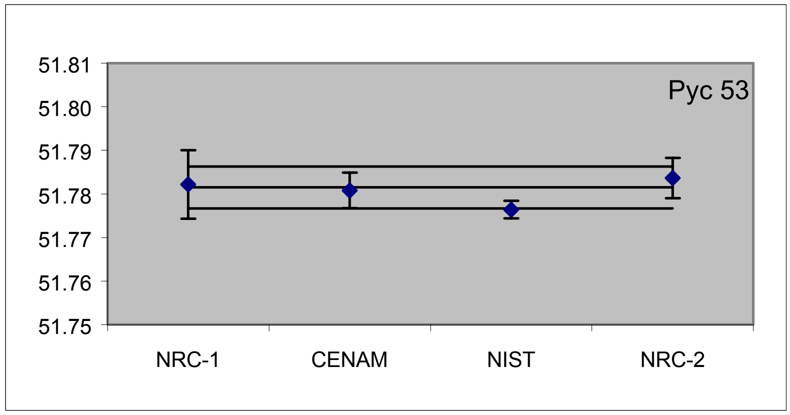
6. References

[1] Patterson, J.B., Morris, E.C., *Metrologia* 1994, **31**, 277-88.

[2] Müller, .J.W, *J. Res. of the NIST* 2000 **105**, 551-5.

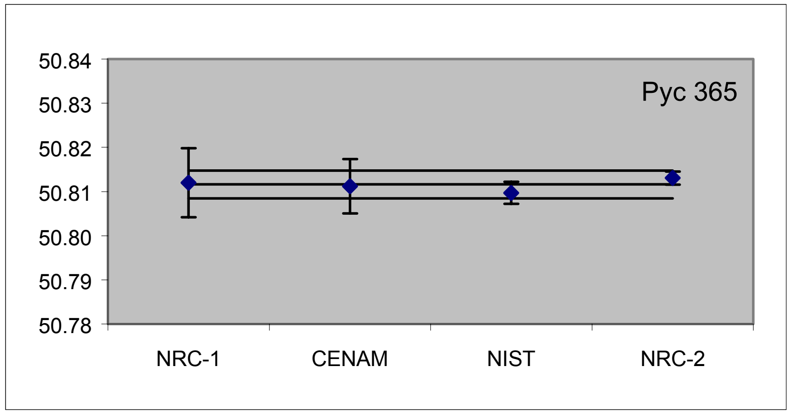
Pyc 53 **50 mL**

Laboratory	Volume	U (95%)	ν
NRC-1	51.7822	0.0078	6.5
CENAM	51.7808	0.0041	27
NIST	51.7764	0.0020	9.0
NRC-2	51.7836	0.0046	2.0
MEDIAN	51.7815	0.0048	3.0



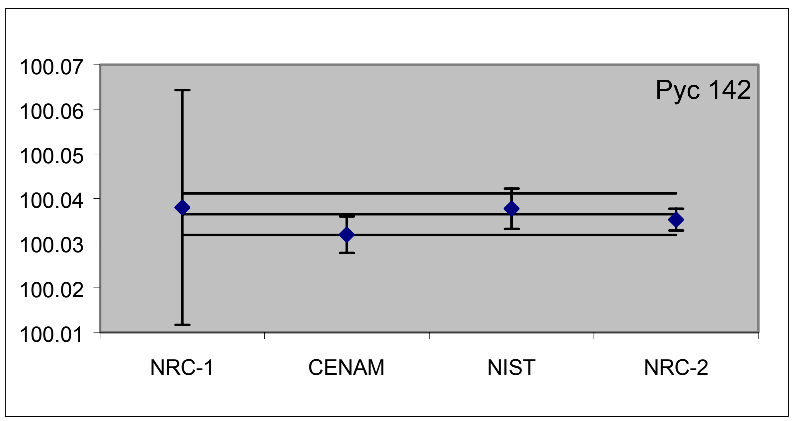
Pyc 365 **50 mL**

Laboratory	Volume	U (95%)	ν
NRC-1	50.8120	0.0078	5.8
CENAM	50.8112	0.0062	25
NIST	50.8097	0.0025	9.0
NRC-2	50.8131	0.0015	11
MEDIAN	50.8116	0.0032	3.0



Pyc 142 **100 mL**

Laboratory	Volume	U (95%)	ν
NRC-1	100.0380	0.0264	1.9
CENAM	100.0319	0.0041	28
NIST	100.0377	0.0045	9.0
NRC-2	100.0353	0.0025	11
MEDIAN	100.0365	0.0047	3.0



Pyc 322 **100 mL**

Laboratory	Volume	U (95%)	ν
NRC-1	99.5050	0.0124	3.8
CENAM	99.4987	0.0062	26
NIST	99.5016	0.0036	9.0
NRC-2	99.5068	0.0044	3.8
MEDIAN	99.5033	0.0088	3.0

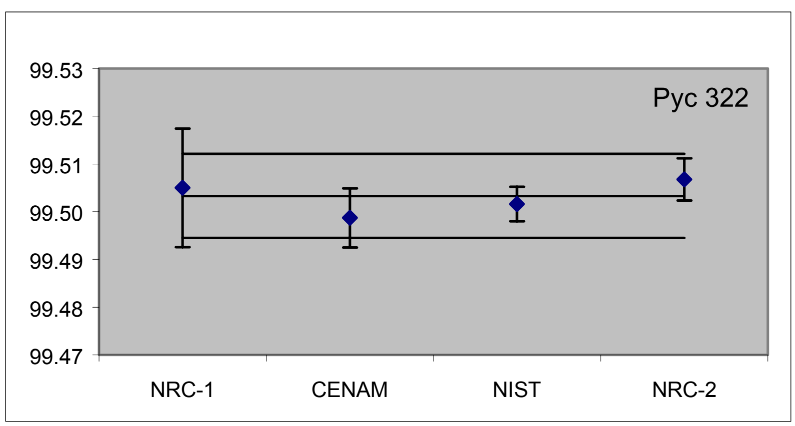


Figure 1: Tables and Graphs of results of the comparisons; ν is the degrees of freedom.

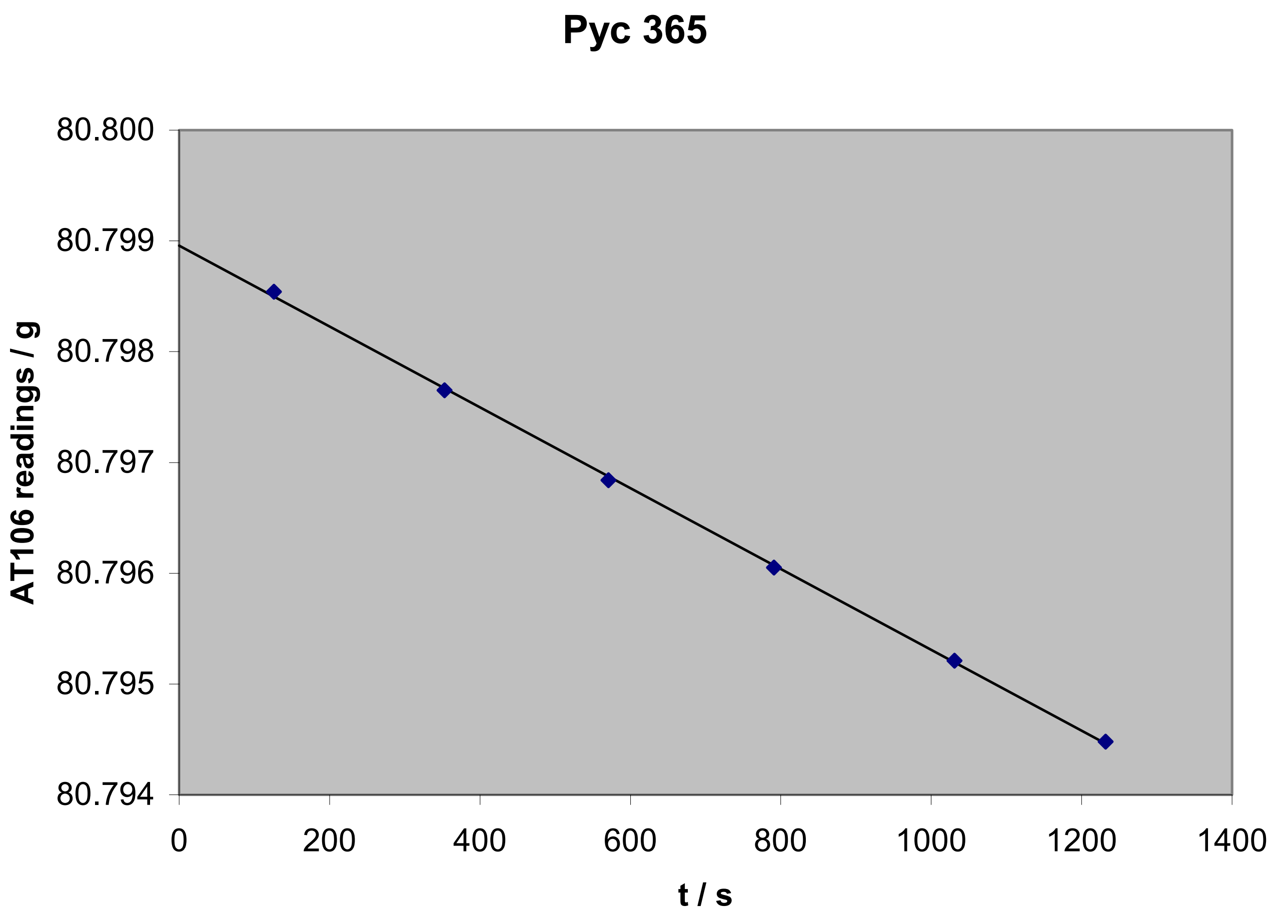


Figure 2 Example of the variation with time of the mass of Pyc365 filled with water; the water is evaporating.