BILATERAL COMPARISON ON THE CALIBRATIONS OF HYDROMETERS FOR LIQUID DENSITY BETWEEN INRIM-ITALY AND INMETRO-BRAZIL - SIM.M.D-S2

Salvatore Lorefice[1], Dalni Malta[2], José Julio Pinheiro[2], Paulo Roberto Marteleto[2]
[1] INRIM Strada delle Cacce, 73 - 91 10135 Torino – Italy
[2] INMETRO, Xerém, Duque de Caxias, Rj. – Brazil

Abstract
The results of the SIM.M.D-S2 bilateral comparison between INRIM – Italy and INMETRO – Brazil are summarized in this report. The aims of this comparison were to check the stated uncertainty levels and the degrees of equivalence between the two Institutes on the calibration of hydrometers for liquid density in the range of 800 kg/m^3 to 1 000 kg/m^3 at 20 ºC, by means of two transfer standards of excellent metrological characteristics.

1. Outline
Under mutual agreement between the National Metrology Institutes of Italy and Brazil respectively (INRIM, *Istituto Naticionale de la Richerca Italiana* and INMETRO, *Instituto Nacional de Metrologia, Normalização e Qualidade Industrial*) agreed to carry out a bilateral comparison based on the calibration of hydrometers for liquid density. Such comparison was registered as the SIM.M.D-S2.
Both institutes had been involved in similar comparisons in their metrological regional organization EURAMET and SIM respectively [1, 2], INRIM also took part in the supplementary comparison designed as SIM.M.D-S1 [3].
The aim of the SIM.M.D-S2 was to harmonize the stated different levels of INMETRO and INRIM laboratories on hydrometers calibration in the density range between 800 kg/m^3 to 1 000 kg/m^3 at 20 ºC. Mr Luis Omar Becerra from CENAM-Mexico has been invited as referee for reviewing the used criterion and possible typing errors or mistakes in the results of the two NMIs.

2. Organization
2.1 Transfer standards (hydrometer samples)
For the comparison the INRIM supplies two hydrometers with the following characteristics:

- S/N. 9135 hydrometer L 20 type (division = 0.2 kg/m^3) manufactured by G.H. Zeal Ltd. (UK) having nominal range of 800 - 820 kg/ m^3
- S/N. 6905 hydrometer L 10 type (division = 0.1 kg/m^3) manufactured by L. Schneider GmbH (Germany) having nominal range of 990 – 1 000 kg/ m^3.

The cubic expansion coefficient for both hydrometers was assumed to be $25\cdot10^{-6}$ °C^{-1} with an uncertainty of $2\cdot10^{-6}$ °C^{-1}, with rectangular distribution.
INRIM calibrated both hydrometers several times, in addition the S/N. 9135 hydrometer has been used as transfer standard in the SIM.M.D-S1 (May 07) and the S/N. 6905 hydrometer in the EUROMET 702/EUROMET.M.D-K4 (March 04).
The results of the calibration performed by INRIM of each hydrometer at each tested stated graduation mark are listed in Table 1. The Table also shows the average of the resulting value and the standard uncertainty due to the reproducibility of the pilot laboratory, u_{rep}. The standard uncertainty due to the reproducibility of INRIM takes into account the stability of the hydrometers, the calculation is based on the difference of the measurements values X of the INRIM as an interval of uniform probability density, according to [4]

$$u_{rep} = \frac{X_{max} - X_{min}}{\sqrt{12}} \qquad 1.$$

Table 1. Results of the calibration of the S/N 9135 and S/N 6905 hydrometers at INRIM in the period March 2004 – March 2010. A new balance has been used in the calibration of March 2010.

S/N. 9135 kg m^{-3}		Data					
		November 06	February 07	May 07	March 10	Average	u_{rep}
802.0	x 10^-2 kg m^-3	-8.2	-7.2	-6.7	-5.1	-6.8	0.9
807.0		-8.8	-7.9	-7.7	-6.6	-7.7	0.6
813.0		-8.6	-7.4	-7.7	-6.2	-7.5	0.7
818.0		-3.9	.-3.1	-3.7	-2.2	-3.2	0.5

S/N. 6905 kg m^{-3}		Data				
		March 04	October 04	March 10	Average	u_{rep}
990.5	x 10^-1 kg m^-3	3.90	3.97	4.00	3.96	0.03
993.5		3.72	3.78	3.81	3.77	0.03
996.5		3.61	3.71	3.74	3.69	0.04
999.5		3.81	3.87	3.97	3.88	0.05

The Table shows that the u_{rep} values for both transfer standards are lower than the usual claimed uncertainty on hydrometer calibration of the INRIM; that main supports the good stability of the two instruments.

2.2 Circulation and date of measurements

The travelling standards were measured first at INMETRO and them at INRIM according to the dates of Table 2.

Table 2. Dates of measurement of the transfer standards.

Acronym	**Date**
INMETRO	December, 2009
INRIM	March, 2010

2.3 Procedure and method of measurement

Both laboratories were asked to calibrate the assigned hydrometers at four graduation marks of the scale and the correction *C* was calculated for each of them at the reference temperature of 20 °C. The test marks and the surface-tension values of the liquid, in which each hydrometer was intended to be used, were stated in advance.

Both laboratories were free to perform all measurements using their own procedure based on hydrostatic weighing.

Both laboratories used the same balance-comparator for the weighing of the hydrometers in air and when they were plugged into the reference liquid. The weighing method was usually the direct reading of the balance; At least 5 weighing sequences were carried out for each hydrometer in air and in the reference liquid at each of the four stated scale readings. The scale readings had to be adjusted to the liquid level such that the middle of the graduation mark was aligned with the horizontal plane of liquid.

Table 3. Summary of the experimental facilities used in the comparison

Institute	Balance Max capacity [g]/readability [g] Weighing in air	Hydrostatic weighing	Buoyant liquid	Thermostat type, capacity	Thermometer for liquid temperature	Alignment	Surface tension method
INRIM	520 / 0.000 01		n-Nonane	Double-walled glass vessel, 30 litre	100 Ohm PRT, ac bridge	CCD camera automatic	Plate
INMETRO	3 000 / 0.00 1		n-Dodecane	Tamson, TV7000LT	100 Ohm PRT, Fluke	Magnifier hand-operated	Plate

Table 3 summarizes the differences in the calibration procedure and in the equipments between the two laboratories.

3. Results

3.1 The reported data

According with the technical protocol, all information concerning the calibration was submitted by participants to the referee of comparison by the sheets Report Form 1 and Report Form 2. The data analysis was related to:

a) Details of the instrumentation used by each participant in the project, including the origin of their traceability to the SI.
b) Details of the relevant information on the measurements and parameters used for the comparison as local gravity, mass measurements, density of working fluid and, finally, the ambient conditions including data on air density, air temperature, air pressure, humidity and CO_2 content.
c) Calculated values of the four corrections for each transfer standard at the specified reading marks and surface tension values.
d) Uncertainty budget of the four calculated corrections, which were estimated and combined following GUM [5] under the responsibility of each participating institute. Each laboratory also reported the uncertainty of all measured quantities as well as the effective degrees of freedom ν_{eff} of the combined standard uncertainty u_c, the t-factor $t_{95}(\nu_{\text{eff}})$ taken from the t-distribution for a 95% confidence level and the expanded uncertainty for the corrections as $U_{95} = t_{95}(\nu_{\text{eff}}) \cdot u_c$

and, finally

e) the consistency within the reported results of both laboratories by the normalized error E

$$E = \frac{\left| X_{\text{INMETRO}} - X_{\text{INRIM}} \right|}{2\sqrt{\left(u(X_{\text{INMETRO}})^2 + u(X_{\text{INRIM}})^2\right)}} \qquad 2$$

where $X_{INMETRO}$ and X_{INRIM} are the corrections for each tested graduation mark of each one of the hydrometers claimed by each laboratory, respectively, $u(X_{INRIM})$ and $u(X_{INMETRO})$ are the related standard uncertainty of corrections.

The normalized error indicates that the difference between the measured value of the participating laboratory and the assigned value of the artefact is less than the combined uncertainties of the artefact and the reference laboratory. If E results between -1 and +1, generally the measured values are considered to have performed an acceptable measurement, and are consistent.

Table 4. Measurements results as reported by INMETRO and INRIM concerning the hydrometers S/N 9135 and S/N 6905, respectively. Last column reports the normalized error for each calibrated graduation marks.

S/N. 9135 kg m^{-3}		NMI INRIM	INMETRO	*E*
802.0	x 10^-2 kg m^-3	-5.13	-5.50	0.10
807.0		-6.59	-8.30	0.44
813.0		-6.19	-8.00	0.47
818.0		-2.17	-3.60	0.37
Combined standard uncertainty of corrections. u_c		1.3	1.5	
Expanded uncertainty of corrections. $U_{95} = t_{95}(n_{eff})\, u_c$		2.5	3.0	
Student t-factor $t_{95}(n_{eff})$		1.97	1.98	

S/N. 6905 kg m^{-3}		NMI INRIM	INMETRO	*E*
990.5	x 10^-2 kg m^-3	40.0	35.4	1.18
993.5		38.1	34.3	0.97
996.5		37.4	34.2	0.83
999.5		39.7	38.7	0.26
Combined standard uncertainty of corrections. u_c		1.2	1.5	
Expanded uncertainty of corrections. $U_{95} = t_{95}(n_{eff})\, u_c$		2.4	3.0	
Student t-factor $t_{95}(n_{eff})$		1.97	1.96	

The corrections with the related uncertainties at the specific temperature of 20 ºC for the two hydrometers as claimed by the two participants are reported in Table 4. The Table also include for each calibrated graduation marks the resulted normalized error *E*.

A satisfactory level of measurement agreement between the two Institutes is resulted in the range 802.0 kg m^{-3} and 818.0 kg m^{-3} (S/N 9135 hydrometer). In the range 990.5 kg m^{-3} and 999.5 kg m^{-3} (S/N 6905 hydrometer) the agreement seems almost contradictory, as the normalized error *E* changes from 0.26 to 1.18. The underestimation of uncertainty of one of the participants could be the cause of this result.

3.2 Re-evaluation of the claimed uncertainty

The claimed standard uncertainty of INRIM for the corrections related to the two hydrometers S/N 9135 and S/N 6905 should be re-considered and increased of 2 and 1 ppm, respectively if the uncertainty of reproducibility of the INRIM measurements given in the Table 1 is considered. The re-evaluated uncertainty of INRIM in which the reproducibility contribution has been taken into account is shown, at 1 σ of confidence level, in Table 5.

Anyway the normalized error *E*, at the density value at the calibrated graduated mark 990.5 kg m^{-3} doesn't result yet within the range -1 and 1 (E=-1.14), even if it has been calculated by increasing the uncertainty of INRIM, that means that the claimed uncertainty of INMETRO laboratory must be re-considered.

The repeatability of the INMETRO measurements could be the main cause of the variability of the agreement on the calibration of the hydrometer S/N 6905. It could be evaluated from the whole

Table 5. Re-evaluation of the claimed uncertainty of INRIM, due to the reproducibility contribution of the calibration of the hydrometers S/N 9135 and S/N6905.

Hydrometer S/N	**Density range** kg m^{-3}	***u*** kg m^{-3}
9135	802.0 ÷ 818.0	$1.5 \cdot 10^{-2}$
6905	990.5 ÷ 999.5	$1.3 \cdot 10^{-2}$

results of calibration obtained on the same hydrometer or it could be calculated from equation (2) fixing that the results of the two laboratories are compatible. According with this last approach, the uncertainty of the INMETRO laboratory results to be not lower than $1.7 \cdot 10^{-2}$ kg/m^3 (at 1 σ) in the range 990,5 kg/m^3 and 999,5 kg/m^3.

3.3 Degree of equivalence between INMETRO and INRIM

The degree of equivalence between INMETRO and INRIM laboratories is calculated as the difference between the values reported by participants

$$d_{INMETRO,INRIM} = X_{INMETRO} - X_{INRIM} \qquad 2$$

with the expanded uncertainty

$$U\left(d_{INMETRO,INRIM}\right) = 2\sqrt{u^2\left(X_{INMETRO}\right) + u^2\left(X_{INRIM}\right)} \qquad 3$$

In Table 6 are listed the degrees of equivalence between INMETRO and INRIM for the selected values resulting from the calibration of the two transfer standards between 800 kg/m^3 and 1 000 kg/m^3. The standard uncertainty of INRIM in the equation 3 takes into account the reproducibility contribution of the repeated measurement made by INRIM, too.

4 Conclusions

The main objective of this SIM comparison was:

- to evaluate the degree of equivalence between INRIM-Italy and INMETRO-Brazil in the calibration of hydrometers of high accuracy within the range of 800 kg/m^3 to 1 000 kg/m^3.

In order to reach such objectives, two hydrometers were measured in both laboratories from December 2009 to March 2010.

For the measurements each laboratory used their own hydrostatic weighing system and procedures.

The results reported by participants show a satisfactory level of agreement between the two Institutes measurements related to the hydrometer calibration in the range between 802.0 kg m^{-3} and 999.5.0 kg m^{-3}. Anyway a weakly agreement mainly due to the underestimation of uncertainty of one of the participants resulted in the range between 990.5 kg m^{-3} and 999.5 kg m^{-3} (S/N 6905 hydrometer).

Table 6. The degrees of equivalence $d_{i,j}$ between pairs of the two NMIs the hydrometers 9135 and 6905, respectively. The table also shows the uncertainty of each value at the 95% confidence level. The calculated uncertainty also takes into account the standard uncertainty due to the reproducibility of INRIM.

Graduation mark g cm^{-3}	$d_{INMETRO-INRIM}$ g cm^{-3}	$U(d_{INMETRO-INRIM})$ g cm^{-3}
0.802 0	-3.70E-06	4.30E-05
0.807 0	-1.71E-05	
0.813 0	-1.81E-05	
0.818 0	-1.43E-05	
0.990 5	-4.57E-05	4.00E-05
0.993 5	-3.79E-05	
0.996 5	-3.23E-05	
0.999 5	-1.03E-05	

Reference

[1] Lorefice, S et al. - EUROMET.M.D-K4 / EUROMET Project 702: Comparison of the calibration of high resolution hydrometers for liquid density determinations – Metrologia, 2008, 45, Tech. Suppl., 07008. EUROMET.M.D-K4 Final Report, 2008.

[2] Becerra L.O - Final report of comparison of the calibrations of hydrometers for liquid density determination between SIM laboratories: SIM.M.D-K4 *Metrologia*, 2009, **46**, *Tech. Suppl.*, 07007.

[3] Becerra L.O., Lorefice S.- Report of the bilateral comparison of the calibrations of hydrometers for liquid density determination between CENAM–Mexico and INRIM–Italy: SIM.M.D-S1 *Metrologia*, 2009, **46**, *Tech. Suppl.*, 07006.

[4] JCGM 100:2008 - Evaluation of measurement data — Guide to the expression of uncertainty in measurement.