COMPARISON OF LIQUID DENSITY MEASUREMENTS AMONG SIM NMIs – SIM.M.D-S7

Final Report

Luis Omar Becerra[1], Sheila Preste[2], Luis Manuel Peña[1]

[1]Centro Nacional de Metrología – CENAM
El Marqués, Querétaro, México

[2]Laboratorio Tecnológico del Uruguay – LATU
Montevideo, Uruguay

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Coordinating institutes: LATU – Uruguay and CENAM – Mexico.

1. Outline

The aim of this comparison was to compare measurement results on liquid density at 20°C and at atmospheric pressure among National Metrology Institutes (NMIs) belonging to the Inter-American Metrology System (SIM, by its acronym in Spanish).

Liquid density is an important quantity for quality control of products, which is highly correlated with specific gravity, alcoholic strength, sugar concentration, of a liquid, by other side, density meters usually are calibrated using liquid densities as reference e. g. by oscillation type density meters among others; that is why for National Metrology Institutes it is very important to support their measurement capabilities on liquid density.

In April and May of 2021, a density questionnaire was circulated among SIM NMIs. An important output of this questionnaire was the need for a measurement comparison of measurement results of liquid density by hydrostatic weighing. For that reason, a SIM comparison of liquid density was planned with the participation of nine NMIs, and for the time required in the preparation of more than one liquid and economic reasons, it was decided to use only one liquid, a Polyalphaolefin.

For this comparison LATU - Uruguay acted as the pilot laboratory and CENAM - México prepared the liquid samples, made the pivot measurements of the liquids as well as the packing and sending the liquid samples to participant laboratories.

CENAM prepared four batches of a liquid (polyalphaolefin) which were measured, divided, and sent to participant laboratories according to their requirements of their hydrostatic weighing systems.

The sample liquid was packaged in 1-litre bottles for sending to participant laboratories and the packed liquid were sent by private courier.

Participant institutes received the liquid sample, and they measured it in their own facilities, hydrostatic weighing system, and measurement procedures.

2. Participant Laboratories

The SIM NMIs participated in this comparison were the following,

Table 1. Participant laboratories

No.	National Institute of Metrology	Acronym	Technical Contact
1	**Laboratorio Tecnológico del Uruguay** Avenida Italia 6201 Montevideo, Uruguay	LATU	Sheila Preste spreste@latu.org.uy Gabriel Almeida galmeida@latu.org.uy
2	**Centro Nacional de Metrología** km. 4,5 Carretera a los Cués, Municipio El Marqués Querétaro, México	CENAM	Luis Omar Becerra lbecerra@cenam.mx César Augusto Mata cmata@cenam.mx
3	**Laboratorio Costarricense de Metrología** 500 m N, 50 m O del Supermercado Muñoz & Nanne, Ciudad de la Investigación, Universidad de Costa Rica, San Pedro de Montes de Oca, Costa Rica	LACOMET	Francisco Sequeira fsequeira@lcm.go.cr Luis Rodríguez lrodriguez@lcm.go.cr
4	**Instituto Nacional de Metrología de Colombia** Av. Carrera 50 No.26-55 Int. 2, Bogotá, Colombia	INM	Luis Carlos Castro lcastro@inm.gov.co Gina Paola Bustos gpabustos@inm.gov.co
5	**Servicio Ecuatoriano de Normalización** Baquerizo Moreno E8-29 y Almagro, Quito, Ecuador	INEN	Víctor Hugo Guevara vguevara@normalizacion.gob.ec Wilson Gallegos wgallegos@normalizacion.gob.ec Wilson Naula wnaula@normalizacion.gob.ec
6	**Instituto Nacional de Calidad** Calle De la Prosa 150, San Borja - Lima 27, Perú	INACAL	Luz Cori Almonte lcori@inacal.gob.pe Donny Taipe dtaipe@inacal.gob.pe
7	**CESMEC Ltda.** Av. Marathon 2595, 781-0552 Macul, Santiago, Chile	CESMEC	Fernando Andres Garcia González fernando.a.garcia@bureauveritas.com Diosimir Rodriguez diosimir.rodriguez@bureauveritas.cl
8	**Instituto Nacional De Tecnología Industrial** Parque Tecnológico Miguelete Avenida General Paz 5445, B1650KNA San Martín – Buenos Aires, Argentina	INTI	Rubén Quille rquille@inti.gob.ar Laura Milena De la Asunción López lasuncion@inti.gob.ar
9	**Instituto Boliviano de Metrología** Av. Camacho No. 1488 - Edificio Anexo – La Paz, Bolivia	IBMETRO	Romer Larico rlarico@ibmetro.gob.bo Mijael Mamani mmamani@ibmetro.gob.bo

3. Measurement systems of the participant laboratories

The density standard and the hydrostatic weighing systems reported by participant laboratories are listed in Table 2.

Table 2. Density standards and the hydrostatic weighing systems of participant laboratories.

NMI	Solid density standard	Balance	Mass standards	Thermostatic bath	Type of operation of the hydrostatic weighing system
CENAM	No brand Zerodur sphere Approx. Mass 1 kg Density 2 533 kg m^{-3} Calibrated by PTB - Germany	Mettler Toledo model AX1005 Max = 1 kg, d = 0.01 mg	Häfner Set of stainless-steel weights class OIML E_2 1 mg – 1 000 g laboratories. Calibrated by CENAM	Manufacturer by CENAM In-house made with external thermostatic control Capacity approx. 60 L Thermal stability +/- 1 mK	Automatic
INM	W.O. Schmidt, Braunschweig fused silica approx. Mass 321 g Density 2 203 kg m^{-3} Calibrated by PTB - Germany	Mettler Toledo model XPE 404S+Max = 410 g, d = 0.1 mg Calibrated by INM - Colombia	---	Tamson TV7000LT Capacity 70 L Thermal stability +/- 5 mK	Manual
LACOMET	Sartorius Silicon sphere Approx. Mass 1 kg Density 2 329 kg m^{-3} Calibrated by PTB - Germany	Mettler Toledo model AT1005 Max = 1 kg, d = 0.05 mg	Sartorius Set of stainless-steel weights class OIML E_2 1 mg – 5 000 g Calibrated by LACOMET	Manufactured by CENAM made with external thermostatic control. Capacity: approx.60 Liters Thermal stability +/- 0.6 mK	Automatic
IBMETRO	W.O. Schmidt, Braunschweig Quartz approx. Mass 218 g density 2 203 kg m^{-3} Calibrated by CEM - Spain	Mettler Toledo, model XS204 Max = 220 g, d = 0.1 mg Calibrated by IBMETRO - Bolivia	---	Thamson Visibility bath Capacity 70 L Thermal stability +/- 23 mK	Manual

NMI	Solid density standard	Balance	Mass standards	Thermostatic bath	Type of operation of the hydrostatic weighing system
INEN	Mettler Toledo – Duran Fused silica Approx. Mass 22.2 g Density 2 220 kg m^{-3} Calibrated by INEN - Ecuador	Mettler Toledo model XP504 Max = 520 g, d = 0.1 mg	Mettler Toledo Set of stainless-steel weights class OIML E_2 1 mg – 5 000 g Calibrated by INEN - Ecuador	Fisher Brand, model CPX2800 Capacity 2.8 liters Thermal stability +/- 1°C	Manual
INACAL	Mettler Toledo Stainless-steel weight Approx. Mass 100 g Density 8 000 kg m^{-3} Calibrated by CEM - Spain	Alemania Max = 220 g, d = 0.1 mg	Mettler Toledo Stainless-steel weighs class OIML E_1 1 mg - 200 g Calibrated by INACAL - Peru	INACAL Capacity 5 L thermal stability +/- 50 mK	Manual
LATU	W.O. Schmidt, Braunschweig fused silica approx. Mass 217 g density 2 203 kg m^{-3} Calibrated by PTB	Mettler Toledo Max = 220 g, d = 0.1 mg Calibrated by LATU – Uruguay		Tamson TLC30 Capacity 5 L Thermal stability +/- 5 mK	Manual
CESMEC	W.O. Schmidt, Braunschweig fused silica approx. Mass 220 g density 2 203 kg m^{-3} Traceability to PTB	Shimadzu Max = 320 g, d = 0.1 mg	Mettler Toledo Set of stainless-steel weights class OIML E_2, 100 g, 2 x 20 g, 1 g Calibrated by CESMEC - Chile	Fluke Thermo-regulated bath Capacity 42 liters Thermal stability +/- 1.3 mK	Manual

NMI	Solid density standard	Balance	Mass standards	Thermostatic bath	Type of operation of the hydrostatic weighing system
INTI	Silicium bearbeitung / Andrea Holm made of zerodur Approx. Mass 1.002 g Density 2 533 kg m^{-3} Calibrated by PTB - Germany	Sartorius Max = 1200 g, d = 0.1 mg	DOLZ HNOS SRL Set of stainless-steel weights class OIML E2 2 g - 500 g INTI - Argentina	Thamson TLC- 15-5 Capacity 5 L Thermal stability +/- 20 mK	Manual

4. Reference Liquid

For this comparison, a volume of **48** litres of a polyalphaolefin was prepared for CENAM. This volume was prepared in 4 batches of 12 litres each.

Each batch was measured by CENAM and was divided and packed in 1 litre bottles for sending to participant laboratories.

The physical characteristics of the reference liquid used are the following:

Surface tension at 20°C: approx. 29 mN m^{-1}
Cubic thermal expansion: approx. 80 x 10^{-5} $°C^{-1}$
Isothermal compressibility: approx. 79 x 10^{-11} Pa^{-1}
Dynamic viscosity: approx. 7.4 mPa s^{-1}

The reference liquid was divided into 4 batches, which were measured by CENAM before being divided and sent to the participant laboratories. CENAM kept 7 litres of batch No. 1 for a second measurement to estimate the density stability of the polyalphaolefin, see Table 3.

The reference liquid was divided and packed in 1 litre bottles to distribute among participant laboratories as follows:

Table 3. Amount of reference liquid sent to participant laboratories

NMI	Amont of liquid (liters)	Batch No.
CENAM	7	1
INM	5	1
LACOMET	8	2
IBMETRO	4	2
INEN	4	3

NMI	Amont of liquid (liters)	Batch No.
INACAL	4	3
LATU	4	3
CESMEC	6	4
INTI	6	4

5. Measurements of the reference liquid

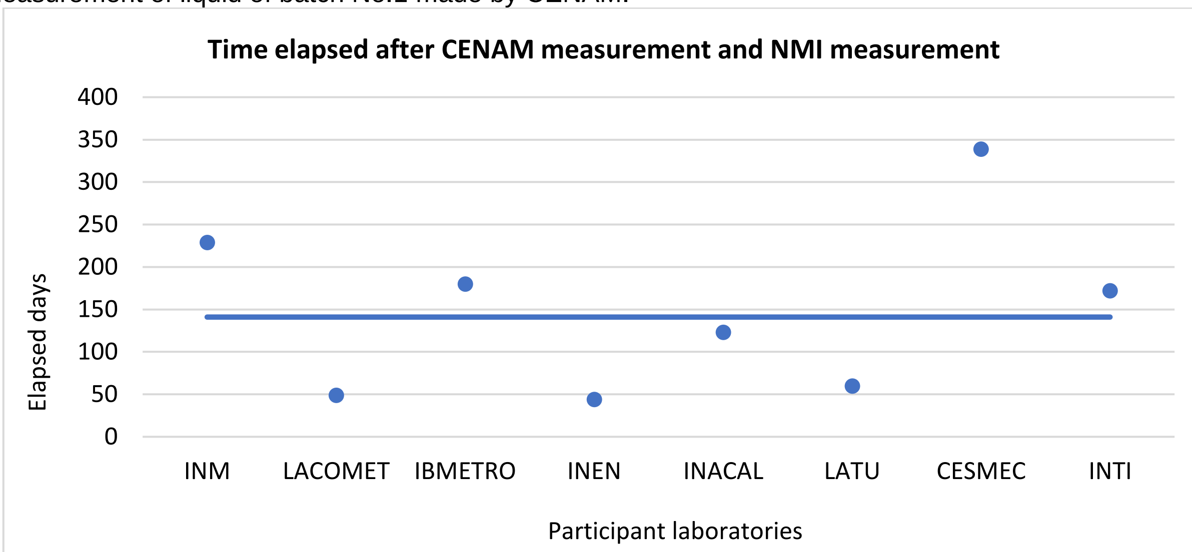
The reference liquid was measured at CENAM before it was sent to participant laboratories.

Table 4. Measurements dates of the reference liquid.

NMI	Batch No. 1	Batch No. 2	Batch No. 3	Batch No. 4	Elapsed days since CENAM's measurement
CENAM	2022-04-20	2022-05-04	2022-05-16	2022-06-06	
INM	2022-12-05				229
LACOMET		2022-06-22			49
IBMETRO		2022-10-31			180
INEN			2022-06-29		44
INACAL			2022-09-16		123
LATU			2022-07-15		60
CESMEC				2023-05-11	339
INTI				2022-11-25	172
CENAM	2022-09-08				**141**

As was mentioned above, to estimate the possible density drift of the reference liquid due to the elapsed time since measurements of CENAM and the NMI, 7 liters of batch No. 1 were kept at CENAM for a control measurement. The CENAM second measurement of batch No. 1 was planned in the protocol of the comparison to be made after measurement dates of participant laboratories. However, due to different circumstances, four NMIs made their measurements after this date and the possible drift of the liquid density was estimated in the same way of the other participants according to the elapsed days from CENAM's measurements, see Fig. 1.

Fig. 1. Time elapsed after CENAM measurement (of the corresponding batch) and the measurement of participant laboratories. The solid line represents the elapsed time between the first and the second density measurement of liquid of batch No.1 made by CENAM.



6. Measurement results of participant laboratories

The measurement results of the reference liquid as reported by participant laboratories are the followings,

Table 5. Measurement results as reported by participant laboratories.
Densities of reference liquid were reported at reference conditions, 20 °C and 101.325 kPa.

NMI	Batch No. 1		Batch No. 2		Batch No. 3		Batch No. 4	
	ρ, kg m^{-3}	u, k=1 kg m^{-3}	ρ, kg m^{-3}	u, k=1 kg m^{-3}	ρ, kg m^{-3}	u, k=1 kg m^{-3}	ρ, kg m^{-3}	u, k=1 kg m^{-3}
CENAM	794.679 9	0.001 8	794.686 5	0.001 8	794.682 9	0.001 8	794.693 4	0.001 8
INM	794.710	0.015 8						
LACOMET			794.695 4	0.002 8				
IBMETRO			794.710	0.019 8				
INEN					794.030	0.084		
INACAL					794.682 0	0.036 2		
LATU					794.765 0	0.012 5		
CESMEC							793.10	0.27
INTI							794.673 7	0.008 8
CENAM [1]	794.693 4	0.001 8						

[1] The second measurement of CENAM for the liquid of batch 1 was used to estimate the possible drift of the reference liquid for all the batches.

As you can noted in Table 4, reference liquid of batch 1 was planned to be measured two times, at the beginning of the comparison and at the end of the comparison, according to the planned schedule of the comparison. However, for different reasons four of the eight NMIs made their measurements after the second measurement of CENAM. No additional problems were reported by participants during the measurements.

7. Estimate of the possible drift of reference liquid

From density measurements of reference liquid of batch No. 1,

Table 6. Estimate of density drift coefficient of the reference liquid.

Date	ρ (kg m^{-3})	$u\rho$, k=1 (kg m^{-3})
2022-04-20	794.679 9	0.001 8
2022-09-08	794.693 4	0.001 8
$\Delta\boldsymbol{\rho}$ (kg m^{-3})	0.013 5	
$\Delta\boldsymbol{time}$ (d)	141	
$\boldsymbol{\delta_{drift}} = \Delta\boldsymbol{\rho}/\Delta\boldsymbol{time}$ (kg m^{-3} d^{-1})	9.6 x 10^{-5}	2.8 x 10^{-5}

The estimated density drift coefficient of the reference liquid is $\delta_{\boldsymbol{drift}} = 9.6 \times 10^{-5}$ kg m^{-3} d^{-1} (kilogram per cubic meter per day). Due to the lack of information, this drift is assumed to be linear along the time, and equal for all the batches even for more than 140 days after CENAM measurements, see Fig. 2.

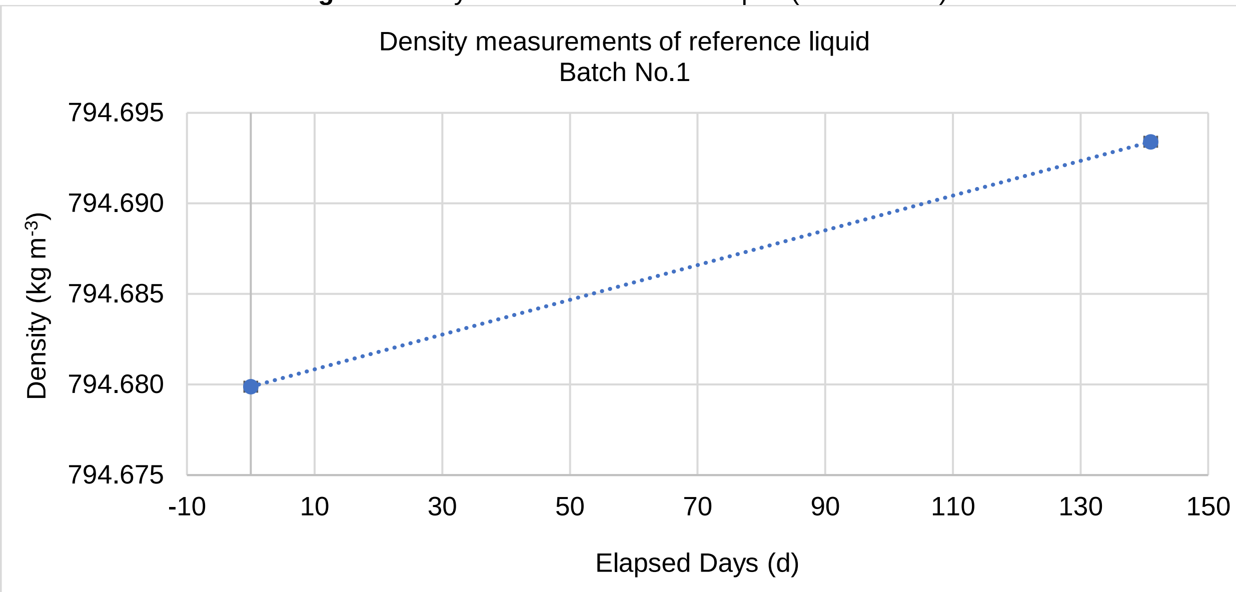
The estimated drift error $\boldsymbol{\varepsilon_{drift\,i}}$, and its associated uncertainty $u(\boldsymbol{\varepsilon_{drift\,i}})$, was calculated for each NMI according to the reported date of measurements.

The uncertainty associated with the error of the drift, was calculated considering the drift as range with a uniform probability density distribution associated with this range.

$$\boldsymbol{\varepsilon_{drift\,i}} = \delta_{\boldsymbol{drift}}\ \Delta time_i \tag{1}$$

$$u(\boldsymbol{\varepsilon_{drift\,i}}) = \frac{\varepsilon_{drift\,i}}{\sqrt{12}} \tag{2}$$

Fig. 2. Density drift of the reference liquid (Batch No. 1).



8. Analysis of measurement results

To compare the density results the density differences, NMI minus CENAM were calculated.

These differences are corrected by the possible drift of the reference liquid due to the time elapsed since the density measurement at CENAM (see Tables 7 and 8).

The density differences between the NMIs results and CENAM and their associated uncertainties are calculated as follows,

$$\Delta\rho(NMI - CENAM) = \rho_{NMI} - \rho_{CENAM} - \boldsymbol{\varepsilon_{drift}} \tag{3}$$

$$u\,\Delta\rho(NMI - CENAM) = \sqrt{u^2(\rho_{NMI}) + u^2(\rho_{CENAM}) + u^2\left(\boldsymbol{\varepsilon_{drift}}\right)} \tag{4}$$

Table 7. Calculation of density differences between NMIs and CENAM results

	Batch No. 1		Batch No. 2		Batch No. 3		Batch No. 4	
	ρ kg m^{-3}	u, k = 1 kg m^{-3}	ρ kg m^{-3}	u, k = 1 kg m^{-3}	ρ kg m^{-3}	u, k = 1 kg m^{-3}	ρ kg m^{-3}	u, k = 1 kg m^{-3}
CENAM	794.679 9	0.001 8	794.686 5	0.001 8	794.682 9	0.001 8	794.693 4	0.001 8
INM - Colombia	794.710	0.015 8						
Δtime (Elapsed days)	229							
ε_{drift}	0.022 0	0.006 3						
Δρ (INM-CENAM)	0.008 2	0.017 1						
LACOMET - Costa Rica			794.695 4	0.002 8				
Δtime (Elapsed days)			49					
ε_{drift}			0.004 7	0.001 4				
Δρ (LACOMET-CENAM)			0.004 2	0.003 6				
IBMETRO - Bolivia			794.710 0	0.019 8				
Δtime (Elapsed days)			180					
ε_{drift}			0.017 3	0.005 0				
Δρ (IBMETRO-CENAM)			0.006 3	0.020 5				
INEN - Ecuador					794.030	0.084		
Δtime (Elapsed days)					44			
ε_{drift}					0.004 2	0.001 2		
Δρ (INEN-CENAM)					-0.657	0.084		
INACAL - Peru					794.682	0.036		
Δtime (Elapsed days)					123			
ε_{drift}					0.011 8	0.003 4		
Δρ (INACAL-CENAM)					-0.012 7	0.036 4		
LATU - Uruguay					794.765 0	0.012 5		
Δtime (Elapsed days)					60			
ε_{drift}					0.005 8	0.001 7		
Δρ (LATU-CENAM)					0.076 3	0.012 7		
CESMEC - Chile							793.10	0.27
Δtime (Elapsed days)							339	
ε_{drift}							0.032 5	0.009 4
Δρ (CESMEC-CENAM)							-1.626	0.270
INTI - Argentina							794.673 7	0.008 8
Δtime (Elapsed days)							172	
ε_{drift}							0.016 5	0.004 8
Δρ (INTI-CENAM)							-0.036 2	0.010 2

Table 8. Density differences between NMIs and CENAM results, and its associated uncertainties

	NMI-CENAM kg m^{-3}	*u*, k=1 kg m^{-3}
$\Delta\rho\ (CENAM - CENAM)$	0.000	0.004
$\Delta\rho\ (INM - CENAM)$	0.008	0.017
$\Delta\rho\ (LACOMET - CENAM)$	0.004	0.004
$\Delta\rho\ (IBMETRO - CENAM)$	0.006	0.020
$\Delta\rho\ (INEN - CENAM)$	-0.657	0.084
$\Delta\rho\ (INACAL - CENAM)$	-0.013	0.036
$\Delta\rho\ (LATU - CENAM)$	0.076	0.013
$\Delta\rho\ (CESMEC - CENAM)$	-1.626	0.270
$\Delta\rho\ (INTI - CENAM)$	-0.036	0.010

The density differences are presented in Fig. 3 and Fig. 4.

Fig. 3. Density differences (NMI – CENAM) and their associated uncertainties (k=2).

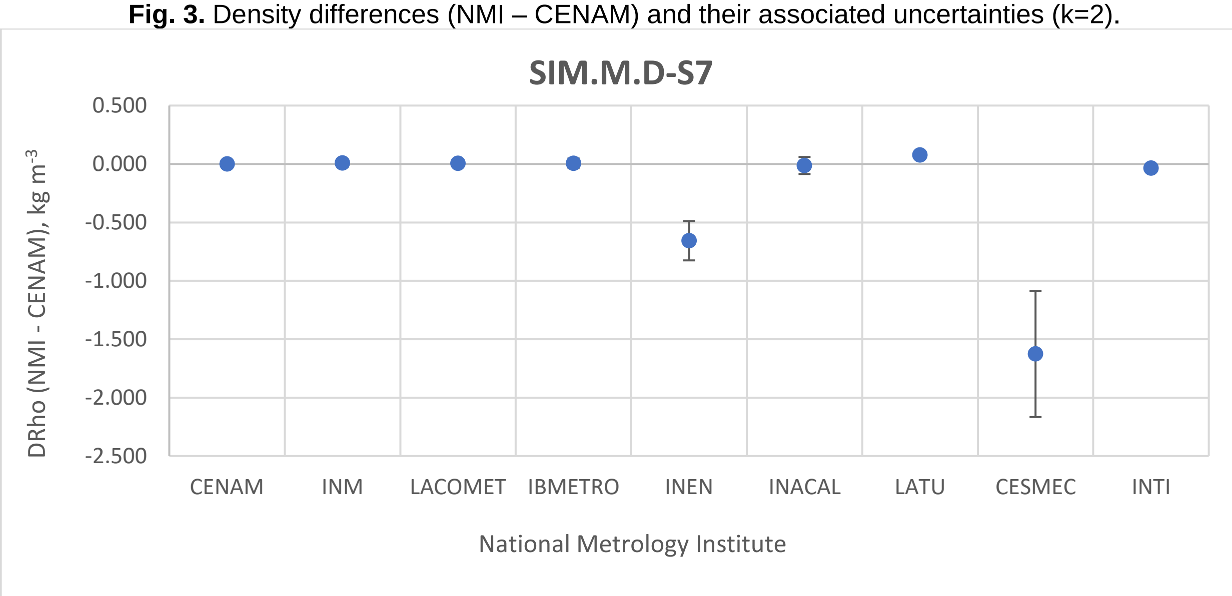
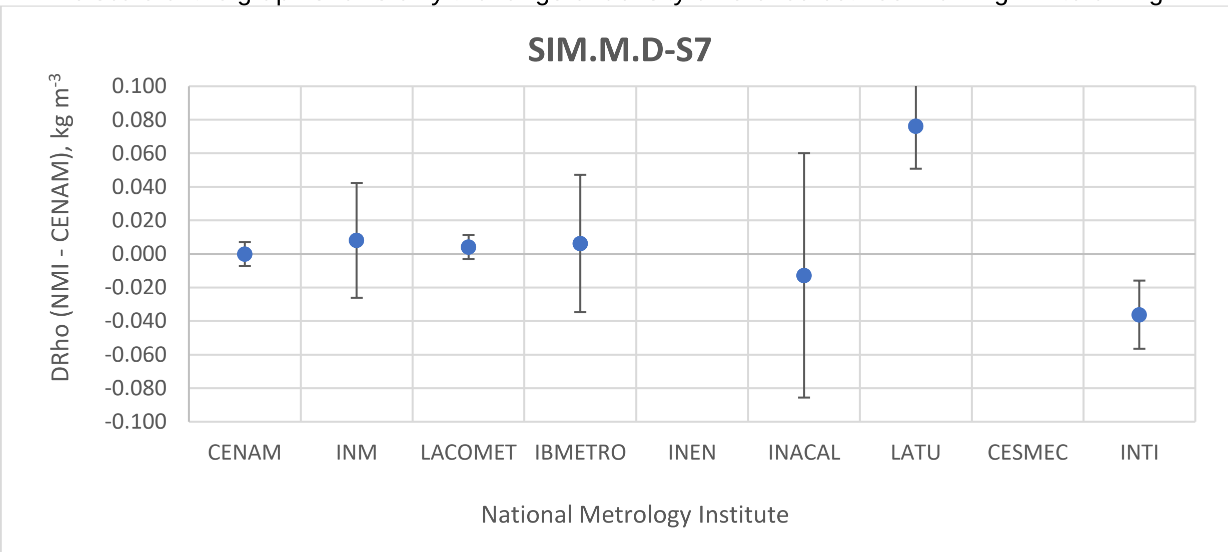


Fig. 4. Density differences (NMI – CENAM) and their associated uncertainties (k=2).
The scale of the graph shows only the range of density difference between -0.1 kg m^{-3} to 0.1 kg m^{-3}



9. Degree of equivalence between participant laboratories

The degree of equivalence between any pair of participant NMIs are calculated by the density differences among them and their uncertainties associated. The density differences of a pair of participant laboratories i and j are calculated as follows,

$$\Delta\rho(NMI_i - NMI_j) = \Delta\rho(NMI_i - CENAM) - \Delta\rho(NMI_j - CENAM) \tag{5}$$

The expanded uncertainties associated to the density differences are calculated with the following expression,

$$U\,\Delta\rho(NMI_i - NMI_j) = 2\sqrt{u^2\,\Delta\rho(NMI_i - CENAM) + u^2\,\Delta\rho(NMI_j - CENAM) - 2u^2(\rho_{CENAM})} \tag{6}$$

Table 9. Density differences between participant laboratories, $\Delta\rho\ (NMI_i - NMI_j)$, kg m^{-3}

	CENAM	INM	LACOMET	IBMETRO	INEN	INACAL	LATU	CESMEC	INTI
CENAM									
INM	0.008								
LACOMET	0.004	-0.004							
IBMETRO	0.006	-0.002	0.002						
INEN	-0.657	-0.665	-0.661	-0.663					
INACAL	-0.013	-0.021	-0.017	-0.019	0.644				
LATU	0.076	0.068	0.072	0.070	0.733	0.089			
CESMEC	-1.626	-1.634	-1.630	-1.632	-0.969	-1.613	-1.702		
INTI	-0.036	-0.044	-0.040	-0.042	0.621	-0.023	-0.112	1.590	

Table 10. Expanded uncertainty associated to density differences between participant laboratories, $U\ \Delta\rho\left(NMI_i - NMI_j\right)$, k = 2, kg m^{-3}

	CENAM	INM	LACOMET	IBMETRO	INEN	INACAL	LATU	CESMEC	INTI
CENAM									
INM	0.034								
LACOMET	0.007	0.035							
IBMETRO	0.041	0.053	0.041						
INEN	0.168	0.171	0.168	0.173					
INACAL	0.073	0.080	0.073	0.083	0.183				
LATU	0.025	0.042	0.026	0.048	0.170	0.077			
CESMEC	0.540	0.541	0.540	0.542	0.566	0.545	0.541		
INTI	0.020	0.039	0.021	0.045	0.169	0.075	0.032	0.541	

To evaluate the consistency of measurement results among participant laboratories, additional to the density differences, the normalized error among participant results were calculated as follows,

$$E_{n\,ij} = \frac{\left|\Delta\rho\left(NMI_i - NMI_j\right)\right|}{U\ \Delta\rho\left(NMI_i - NMI_j\right)} \tag{7}$$

The criterion of the normalized error is the following,

$E_{n\,ij} \leq 1$ results are consistent among them with a confidence level of approximated 95 %.

$E_{n\,ij} > 1$ results are not consistent among them with a confidence level of approximated 95 %.

The normalized errors calculated for each pair NMIs are presented in table 11.

Table 11. Normalized errors calculated among results declared by participant laboratories, E_n, (approx. 95 % of confidence level)

	CENAM	INM	LACOMET	IBMETRO	INEN	INACAL	LATU	CESMEC	INTI
CENAM									
INM	0.24								
LACOMET	0.58	0.11							
IBMETRO	0.15	0.04	0.05						
INEN	3.91	3.88	3.93	3.84					
INACAL	0.17	0.26	0.23	0.23	3.52				
LATU	3.00	1.61	2.77	1.46	4.32	1.16			
CESMEC	3.01	3.02	3.02	3.01	1.71	2.96	3.15		
INTI	1.78	1.12	1.93	0.93	3.67	0.31	3.49	2.94	

10. Conclusions

This supplementary comparison of liquid density was agreed upon with the participation of nine National Metrology Institutes. LATU and CENAM acted as pilot and copilot laboratories respectively for this comparison. This supplementary comparison is the first comparison of liquid density measurements organized within the SIM region.

CENAM prepared the transfer liquid, made the reference measurements and the sent the sample liquid to participant laboratories. CENAM results were used as a pivot to compare the measurement results among participants. Participants measured the liquid density from April 2022 to May 2023.

Even when the planned scheme of measurements was that each participant NMI make the liquid density measurements as soon as they received the sample liquids, to avoid the influence of the density drift of the sample liquid, for different reasons (including customs formalities of the participant countries), some NMIs must delay their measurements for more than six months and one of them for almost a year. However, the possible density drift was included for each participant laboratory.

Each participant laboratory made their liquid density measurements in their own measurement system (hydrostatic weighing system) and density standard. All participant laboratories were required to report the density of the sample liquid to 20 °C and 101.325 kPa.

From density results reported by participant laboratories, 36 density differences between pairs of density results reported by NMIs were calculated and taken to CENAM results as pivot measurements. From the density differences, only 12 were consistent among them, and 24 were not consistent among them. The consistency of each density difference of pair of results reported by the NMIs was evaluated with normalized error criterion, see (7).

References

[1] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, OIML, Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement, Joint Committee for Guides in Metrology, JCGM 100, 2008.

[2] Bettin H. et al. Final report on CCM key comparison CCM.D-K2: Comparison of liquid density standards, 2013, Metrologia, 2013, 50, Tech. Suppl., 07006.