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DENSITY DETERMINATION OF THE WATER PRODUCED AT CENAM BY THE USE OF SOLID DENSITY STANDARDS

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Abstract: This paper presents the results obtained from density measurements of pure water produced at CENAM. This water is used as density standard for calibrations services.

The measurements were done into a scheme of experimental design in order to find possible sources of variability in the hydrostatic weighing system of the national density standard. The design factors checked were: days after the water is produced, positions of the solid density standards at the hydrostatic weighing system and the spheres used.

The variable of interest for the scheme of experimental design was the difference between the water density measured using the solid density standards and the water density calculated by the formula of M. Tanaka et al. [1].

The goal of this study is to estimate an uncertainty value associated to the water density used at CENAM calculated by the formula which includes the storage effect, and by other side evaluating the effects due to the spheres and positions of the sphere into the hydrostatic weighing system of the national density standard.

Keywords: Density, Water density, Solid density standards.

1. INTRODUCTION

The water density is used at CENAM as a reference for density and volume calibrations, and from this work it was estimated an uncertainty for the water density produced at CENAM those calibrations. Additionally the solid density standards and their positions in the hydrostatic weighing system were evaluated in order to characterize them.

The water density used at CENAM is usually calculated by the formula of M. Tanaka et al. [1] "Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports". This formula will be identified in this work as CCM formula because it was developed within the density working group of CCM.

For normal calibration services at CENAM, a relative uncertainty of 1x10^{-5} (k=1) is associated to the water density calculated by the CCM formula. Last value is a conservative value due to the water can be contaminated very easily.

The water type I ASTM [12] used at CENAM for the density and volume services (and others services too) is obtained from devices brand Milli-Pore. The electrical resistivity of the water produced by Milli-Pore devices is about 18,2 MΩ cm, but it is necessary to confirm in one hand that water density uncertainty for the services at CENAM is not underestimated with the risk of report results out of the confidence intervals, and in the other hand do not overestimate it unreasonably.

2. DENSITY STANDARDS

Two spheres of zerodur and one of optical glass were used as solid density standards. The couple of zerodur spheres are the national density standard of Mexico.

The data of the solid density standards are in table 1,

Table 1. Data of solid density standards

Identification	Z-01	Z-02	BK7
Material	Zerodur	Zerodur	Optical glass
Approx. diameter (cm)	9,092	9,102	9,141
Volume (cm^3)	393,593 65	394,850 82	399,917 97
Unc. k=2 (cm^3)	0,000 80	0,000 80	0,000 80
Mass (g)	998,148 18	1 001, 334 00	1 002,974 22
Unc. k=2 (g)	0,000 25	0,000 25	0,000 25
Thermal expansion coefficient (ºC^{-1})	0 x 10^{-6}	0 x 10^{-6}	7 x 10^{-6}
Compressibility coefficient (Pa^{-1})	10,99 x 10^{-10}	10,99 x 10^{-10}	13,51 x 10^{-10}
Traceability	PTB	PTB	PTB

3. HYDROSTATIC WEIGHING SYSTEM

The measurement system used was the national density standard system, which consists in a balance, a thermostatic bath, an automatic handler system for weighing in air and an automatic handler system for weighing in liquid (see fig. 1).

The system for the weighing in liquid has three position aligned in a vertical arrange, where each sphere is weight by comparison against mass standards.

Fig. 1. Hydrostatic weighing system of the national density standard

Mass standards are placed on the pan of the balance by the automatic handler for the weighing in air.

All environmental conditions are registered automatically in the computer as well as the readings of the balance.

4. FORMULA FOR THE WATER DENSITY

The CCM formula for calculation of the water density is the following,

$$\rho_{CCM} = \left\{ a_5 \left[1 - \frac{(t+a_1)^2 (t+a_2)}{a_3 (t+a_4)} \right] + C_{ad} \right\} \cdot F_c \qquad (1)$$

where

t temperature in °C

a_1 = -3,983 035 °C

a_2 = 301,797 °C

a_3 = 522 528,9 °C2

a_4 = 69,348 81 °C

a_5[1] = 999,971 40 kg·m-3

The compressibility correction factor (Fc), is calculated from formula 2,

$$F_c = \left[1 + \left(K_0 + K_1 t + K_2 t^2 \right) \left(p - p_0 \right) \right] \qquad (2)$$

where,

p	atmospheric pressure, Pa
p_0	pressure of reference (101 325 Pa)

$K_0 = 50{,}74 \times 10^{-11}\ \mathrm{Pa}^{-1}$

$K_1 = -0{,}326 \times 10^{-11}\ \mathrm{Pa}^{-1} \cdot {}^{\circ}\mathrm{C}^{-1}$

$K_2 = 0{,}004\ 16 \times 10^{-11}\ \mathrm{Pa}^{-1} \cdot {}^{\circ}\mathrm{C}^{-2}$

As the water was not degassed, the correction for the dissolved air in water (C_{ad}) was calculated using next formula,

$$C_{ad} = s_0 + s_1 t \qquad (3)$$

where,

$s_0 = -4{,}612 \times 10^{-3}\ \mathrm{kg \cdot m^{-3}}$

$s_1 = 0{,}106 \times 10^{-3}\ \mathrm{kg \cdot m^{-3} \cdot {}^{\circ}C^{-1}}$

5. WATER DENSITY MEASUREMENT USING SOLID DENSITY STANDARDS

The water density was measured using the solid density standard by hydrostatic weighing, where the buoyancy of the solid density standard is measured in a balance by comparison against weights (mass standards).

The formula used to calculate the water density is the following,

$$\rho_{EXP} = \frac{m_S - m_p + \rho_a V_p \left[1 + \alpha_p (t - t_0) \right] - \Delta_m - C_g}{V_S \left[1 + \alpha_S (t - t_0) \right] \left[1 + \beta_S (p_S - p_0) \right]} \qquad (4)$$

where

ρ_{EXP}	water density measured experimentally (using solid density standards)
m_S	mass of the sphere
m_p	mass of the weight
ρ_a	air density
V_p	volume of the weight
α_p	thermal expansion coefficient of the stainless steel (weights)
t	temperature of the water
t_0	temperature of reference (20 ºC)
Δ_m	mass difference (read in the balance)
C_g	gravity correction
V_S	volume of the solid density standard
α_S	thermal expansion coefficient of the solid density standard
β_S	compressibility coefficient of the solid density standard
p_S	pressure over the solid density standard
p_0	pressure of reference (101 325 Pa)

6. SCHEME OF MEASUREMENTS

Density of the water calculated by (1) was compared against the density value measured with the solid density standards and calculated by (4). Both density values were compared in order to check the following factor of the hydrostatic weighing system,

a. Number of days after produced the water

b. Density standard used

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[1] a_5 was calculated using the values of isotopic abundance of CENAM's water. The isotopic abundance of CENAM's water was measured at IMTA (Instituto Mexicano de Tecnología del Agua).

c. Position of the sphere within the hydrostatic system

These factors were evaluated by a scheme of experimental design where these factors had different levels.

Table 2. Scheme of experimental design

FACTOR	Id.	Levels
Day after production of the water	A	day 2, day 3, day 4, day 5[2]
Sphere	B	Z-01, Z-02, BK7
Position	C	Top (X1), Medium (X2) Bottom (X3)

For each factor were taken 4 series of 6 comparisons each. There were 144 density differences as total.

It was obtained a unique value for each level of factors (this vale is the sum of the four differences of each level) in order to make the Analysis of Variance (ANOVA).

7. RESULTS OF THE EXPERIMENTS

The ANOVA table (table 3) is obtained from the experimental design of factorial type 3 x 3 x 4

where,

SS	sum of squares ($kg^2 \cdot m^{-6}$)
DF	degrees of freedom
SM	squares mean ($kg^2 \cdot m^{-6}$)
F_0	statistic F,
p-value	significance level value

For this experiment the significance level was defined as $\alpha = 0{,}05$.

The criterion for a significant effect is evaluated according to the next expression,

p-value $\geq \alpha$ the effect is not significant
p-value $< \alpha$ the effect is significant

Table 3. ANOVA table for the water density differences.

Factors	SS	DF	SM	F_0	p-value	
A	$4{,}35 \times 10^{-5}$	3	$1{,}45 \times 10^{-5}$	2,87	**0,04**	significant
B	$5{,}00 \times 10^{-5}$	2	$2{,}50 \times 10^{-5}$	4,94	**0,01**	significant
C	$2{,}15 \times 10^{-5}$	2	$1{,}07 \times 10^{-5}$	2,12	0,12	no significant
AB	$1{,}50 \times 10^{-5}$	6	$2{,}50 \times 10^{-6}$	0,49	0,81	no significant
AC	$2{,}18 \times 10^{-5}$	6	$3{,}64 \times 10^{-6}$	0,72	0,64	no significant
BC	$7{,}17 \times 10^{-5}$	4	$1{,}79 \times 10^{-5}$	3,54	**0,01**	significant
ABC	$6{,}95 \times 10^{-5}$	12	$5{,}80 \times 10^{-6}$	1,15	0,33	no significant
Error	$5{,}46 \times 10^{-4}$	108	$5{,}06 \times 10^{-6}$			
Total	$8{,}40 \times 10^{-4}$	143				

Figure 2 shows the mean differences respect to the day of measurement.

Fig. 2. Graph of mean water density differences in relation with the day of measurement.

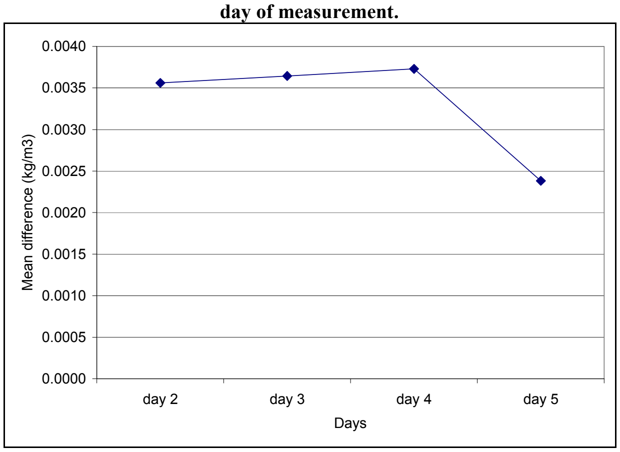
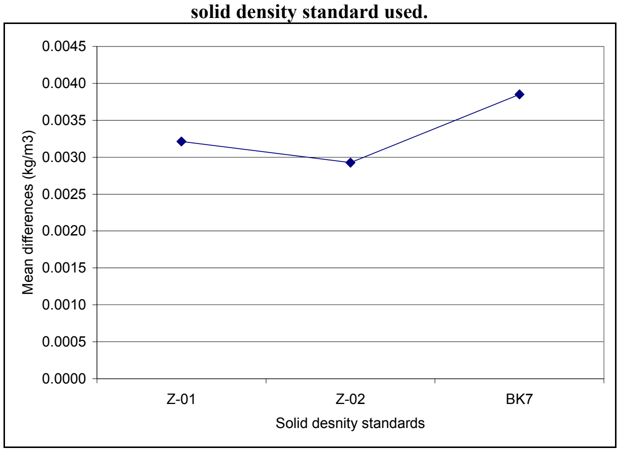


Figure 3 shows the mean difference respect to the solid density standard.

Fig. 3. Graph of mean water density differences in relation with the solid density standard used.



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[2] Day 1 for each week was used for the thermal stabilization of the hydrostatic system.

Figure 4 shows the mean difference respect to position of the hydrostatic weighing system.

Fig. 4. Graph of mean water density differences in relation with the position of the hydrostatic weighing system.

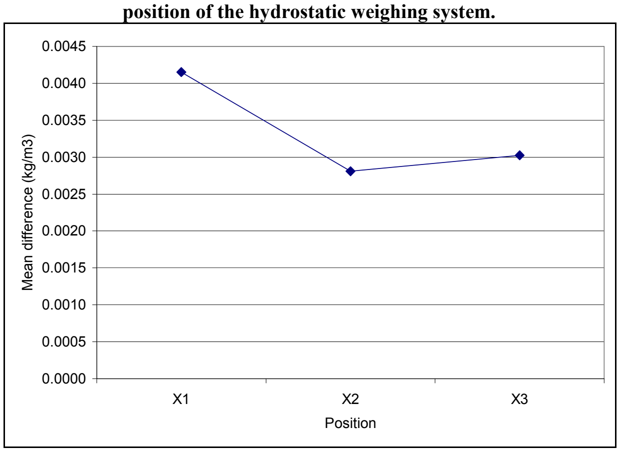
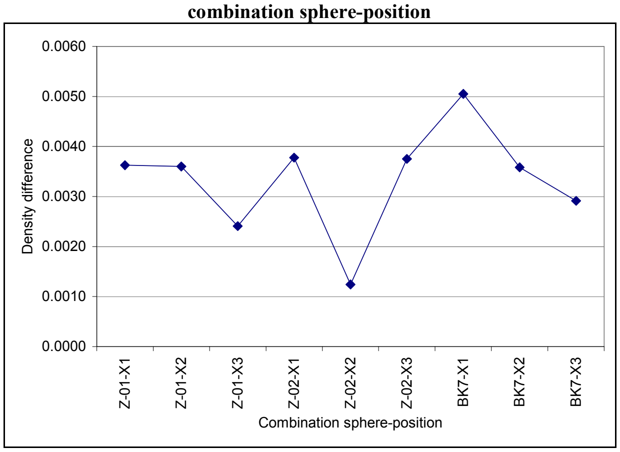


Figure 5. shows the effect of the combination sphere and position of the hydrostatic weighing system.

Fig. 5. Graph of mean water density differences for the combination sphere-position



The mean difference between values of water density calculated by CCM formula and the water density measured with the solid density standards is,

$$\Delta\rho = \rho_{EXP} - \rho_{CCM} = 0{,}003\,3 \text{ kg/m}^3$$

The uncertainties of the water density values and the standard deviation for the 144 differences are,

$$u(\rho_{CCM}) = 0{,}001\,7 \text{ kg/m}^3 \text{ k=1}$$
$$u(\rho_{EXP}) = 0{,}001\,1 \text{ kg/m}^3 \text{ k=1}$$
$$s(\Delta\rho) = 0{,}002\,4 \text{ kg/m}^3$$

Using the normalized error criterion (*En*) in order to compare the consistency of both values at an interval of approximately 95% of confidence, it results,

$$E_{n(\approx 95\%)} = \frac{\Delta\rho}{2\cdot\sqrt{u_{\rho EXP}^2 + u_{\rho CCM}^2 + \dfrac{s(\Delta\rho)^2}{n}}} = 0{,}82 \tag{5}$$

where,

$E_{n(\approx 95\%)}$	normalized error with approx. 95% of confidence level
$u_{\rho EXP}$	standard uncertainty of the water density measured with the solid density standards
$u_{\rho CCM}$	standard uncertainty of the water density calculated with the CCM formula
s	standard deviation of the water densities.
n	number of water density differences

Last value for the normalized error means that such difference is within the confidence interval of the expanded uncertainty of this difference.

8 CONCLUSIONS

ANOVA study throws that the sphere used (solid density standard) as well as the combination of sphere and position are factors that have to be taken into account for the density measurements using the hydrostatic weighing system of the national density standard. The best combination sphere-position is,

Table 4. Best combination sphere-position

Position	Sphere
X1 (top)	Z-01
X2 (mean)	Z-02
X3 (bottom)	BK7

More over, days after the water is produced is another factor to take into account for the density measurements using the water density as a density reference.

On one hand, as the mean density difference is significant respect to the uncertainty of the formula itself [1], and on the other hand, the uncertainty used for the water density for the normal calibration services at CENAM is to large ($1\text{x}10^{-5}$). For CENAM's calibration services it is necessary to estimate an uncertainty value associated to the water density calculated by CCM formula which consider this difference.

In order to consider this difference the proposed uncertainty for the water density evaluated by the CCM formula for the water produced at CENAM is calculated from the next expression,

$$u(\rho) = \sqrt{\frac{\Delta\rho^2}{12} + u(\Delta\rho)^2} = 0{,}002\,2 \text{ kg/m}^3 \tag{6}$$

$$u(\Delta\rho) = \sqrt{u^2_{\rho EXP} + u^2_{\rho CCM} + \frac{s(\Delta\rho)^2}{n}} \qquad (7)$$

Last uncertainty expressed as relative uncertainty is $u(\rho)_{rel} = 2{,}2\text{x}10^{-6}$.

This uncertainty value could be increased due to uncertainties of the input quantities of the CCM formula (mainly pressure and temperature).

With the use of last uncertainty value associated to the water density used at CENAM and calculated by the CCM formula, It will possible to reduce the calibration uncertainty for the density and volume services offered by CENAM.

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