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MEXICAN DENSITY STANDARD: DATA TREATMENT IN HYDROSTATIC WEIGHING

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Abstract: The Mexican Density Standard is starting operation as a national reference. In the present paper, it is presented the data analysis in hydrostatic weighing, the uncertainty estimation and its validation by Monte Carlo's Method of the transfer of accuracy of the National Density Standard of Mexico.

Keywords: Density, Uncertainty

1. HYDROSTATIC WEIGHING SYSTEM

The Mexican Density Standard is a couple of zerodur spheres (calibrated by comparison against two primary density standards) placed in a semi automatic vertical system where the standards are being placed both in the bottom and on the top of the system (see fig 1). For the density determination of an unknown sphere (as an example) we make two weighing sequences in air and in liquid (transfer liquid, pentadecane).

All the spheres are compared against stainless steel weights in order to reduce the no-linearity of the balance. For air weighing the unknown sphere is placed over the balance and, for weighing in liquid the unknown sphere is placed below the balance between the two density standards placed over and below the unknown sphere in order to measure the liquid density and from this way to measure the volume of the sphere under calibration by a measure of the buoyancy effect over this sphere.

The pan of the balance was modified to receive the sphere under test for the air weighing, and there is a suspension with three places for each sphere, two density standards and the sphere under test. The suspension system for liquid weighing is connected to the balance (below the balance).

For the air weighing almost all the process is manual except the data gathering, because the computer takes all the readings from the environmental sensors and from the balance when the metrologist push a button of the balance.

Fig. 1. Hydrostatic Weighing System for the Mexican Density Standard

Fig. 2. Hydrostatic Weighing System. Thermostatic bath with the national density standards in the top and in the bottom and the sphere under test in the middle.

2. SEQUENCE OF THE PROCESS

For a density determination of a solid, a sphere for instance, the sequence of the process is the following,

2.1. Cleanness of the sphere under test (unknown sphere)
2.2. Stabilization time (near of the balance)

2.3. Air weighing (against weights)
2.4. Immerse the sphere under test into the transfer liquid in the corresponding place of the vertical system (into the thermostatic bath). The other two sphere must to be placed in their respectively positions of the vertical systems and, in thermal equilibrium
2.5. Stabilization time (immersed in the liquid)
2.6. Weighing of the spheres immersed in the transfer liquid by comparison against mass standards, one by one
2.7. Getting out the test sphere from the liquid
2.8. Repeat all the process for reproducibility evaluation

3. MODEL OF MEASUREMENT

The model of the measurement is formed by two equations, the first one for the weighing in air and the second one for the weighing in liquid.

The volume of the unknown sphere will have traceability to the solid density standards (zerodur spheres) through the density of the liquid measured at the level of both solid density standards, see (1),

$$\rho_L = \frac{m_S - m_{ms} + \rho_a \cdot V_{ms}\left[1 + \alpha_{ms}(t - t_0)\right] \cdot \left[1 - \beta_{ms}(p - p_0)\right] - \Delta m - g_c}{V_S\left[1 + \alpha_s(t_L - t_0)\right] \cdot \left[1 - \beta_s(p - p_0)\right]} \tag{1}$$

where,

ρ_L	density of the liquid at the level of the density standard
ρ_a	air density
m_s	mass of the sphere (density standard)
m_{ms}	mass of the weights (mass standards)
V_s	volume of the sphere (density standard)
V_{ms}	volume of the weights
Δm	mass difference reading from the balance and corrected by the sensitivity
g_c	gravity correction due to the height difference between gravity centers of both sphere and weights
t	air temperature
t_L	liquid temperature near of the density standard
t_0	reference temperature
p	pressure at level of the density standard
p_0	reference pressure
α_s	volume thermal expansion coefficient of the density standard at 20 °C
α_{ms}	volume thermal expansion coefficient of the weights at 20 °C
β_s	isothermal compressibility coefficient of zerodur at 20 °C and 101,325 kPa
β_{ms}	isothermal compressibility coefficient of stainless steel at 20 °C and 101,325 kPa

from these values of density of the liquid (both top and bottom), and considering a linear vertical gradient for the density of the transfer liquid, we can evaluate the density of the liquid at level of the sphere under test, see (2)

$$\rho_{LT} = \left(\frac{\rho_{L2} - \rho_{L1}}{h_2 - h_1}\right)(h_T - h_1) + \rho_{L1} \tag{2}$$

where,

ρ_{LT}	density of the liquid at the level of the sphere under test
$\rho_{L1,2}$	density of the liquid at the level of the density standards, top or bottom
h_T	distance from the sphere under test to the transfer liquid level
$h_{1,2}$	distance from the solid density standards to the transfer liquid level

With this value now we can evaluated the volume of the sphere under test solving both weighing equations in air and in liquid,

$$V_T = \frac{m_{ms1} - m_{ms2} - \rho_{a1}V_{ms1}Y_1Z_1 + \rho_{a2}V_{ms2}Y_2Z_2 + \Delta m_1 - \Delta m_2 + g_{c1} - g_{c2}}{\rho_{LT}Y_{T2}Z_{T2} - \rho_{aT}Y_{T1}Z_{T1}} \tag{3}$$

where Y_i and Z_i are the corresponding temperature and pressure correction,

$$Y_i = 1 + \alpha_i(t - t_0) \tag{4}$$

$$Z_i = 1 - \beta_i(p - p_0) \tag{5}$$

4. UNCERTAINTY EVALUATION

For the uncertainty evaluation it is necessary to take into account all sources of uncertainty and its sensitivity coefficient related with the volume of the sphere under test.

The formula for the uncertainty evaluation for uncorrelated input variables is the following [1],

$$u_c(y) = \sqrt{\sum_{i=1}^{N}\left[\frac{\partial f}{\partial X_i} \cdot u(x_i)\right]^2} \tag{6}$$

5. NUMERICAL EXAMPLE

A numerical example for the volume measurement of a solid is presented in table 1. The uncertainty analysis was made considering all input quantities uncorrelated.
The first column shows the input quantity, second column shows the mean value, the third column shows the uncertainty of this quantity, in the fourth column are the units, in the fifth column are the contribution of each input quantity to the corresponding intermediate quantity, in the sixth column are the contribution in variance of each input quantity to the intermediate quantities and in the last column are the degrees of freedom estimated for each input quantity according to the GUM [1].

Table 1. Uncertainty budget for a volume of a solid measurement using solid density standards. All input quantities are considered uncorrelated.

Liquid density 1	Value	Uxi		CiUxi	(CiUxi)^2	d.f.
mass of the density standard	998.14818	0.000125	g	3.17586E-07	1.0086E-13	100
volume of the density standard	393.59365	0.0004	cm3	-7.81004E-07	6.0997E-13	100
volume thermal expansion coefficient of the density standard	1.50E-07	1.50E-09	/ºC	6.14796E-11	3.7797E-21	22
compressibility coefficient of the density standard	1.10E-11	1.10E-13	/Pa	-1.42039E-09	2.0175E-18	22
mass of the weights	695.761085	0.000071	g	-1.80262E-07	3.2494E-14	100
volume of the weights	87.4761	0.071	cm3	1.72628E-07	2.9800E-14	100
volume thermal expansion coefficient of the weights	4.80E-05	4.80E-07	/ºC	-1.53095E-10	2.3438E-20	22
air temperature	21.5	0.2	ºC	2.04969E-09	4.2012E-18	100
liquid temperature	20.053	0.006	ºC	-6.93699E-10	4.8122E-19	100
air density	0.00095355	7.30E-07	g/cm3	1.62173E-07	2.6300E-14	114
mass difference	-4.22E-03	8.62E-05	g	-2.19033E-07	4.7976E-14	59
gravity correction	-0.000357453	3.57E-06	g	9.08178E-09	8.2479E-17	13
pressure over the density standard	84507.25	100	Pa	-8.44577E-10	7.1331E-19	22
	0.7684957	g/cm3			9.21E-07	185
Liquid density 2						
mass of the density standard	1001.334	0.000125	g	3.16575E-07	1.0022E-13	100
volume of the density standard	394.85082	0.0004	cm3	-7.78515E-07	6.0608E-13	100
volume thermal expansion coefficient of the density standard	1.50E-07	1.50E-09	/ºC	6.14796E-11	3.7797E-21	22
compressibility coefficient of the density standard	1.10E-11	1.10E-13	/Pa	-1.42039E-09	2.0175E-18	22
mass of the weights	697.9781326	0.000075	g	-1.90072E-07	3.6127E-14	100
volume of the weights	87.7542	0.077	cm3	1.85941E-07	3.4574E-14	100
volume thermal expansion coefficient of the weights	4.80E-05	4.80E-07	/ºC	-1.53095E-10	2.3438E-20	22
air temperature	20.5	0.20	ºC	2.07414E-09	4.3020E-18	100
liquid temperature	20.049	0.0060	ºC	-6.92444E-10	4.7948E-19	100
air density	0.000957823	7.39E-07	g/cm3	1.64219E-07	2.6968E-14	114
mass difference	2.08E-04	1.10E-04	g	-2.78134E-07	7.7358E-14	59
gravity correction	-0.000274278	3.57E-06	g	9.08178E-09	8.2479E-17	13
pressure over the density standard	82380.39	100	Pa	-8.44573E-10	7.1330E-19	22
	0.7684926	g/cm3			9.39E-07	199
Liquid density at solid level						
liquid density 1	0.7684957	9.2E-07	g/cm3	4.76144E-07	2.2671E-13	185
liquid density 2	0.7684926	9.4E-07	g/cm3	4.53234E-07	2.0542E-13	199
distance from sphere1 to liquid level	0.44	0.005	m	-2.79548E-08	7.8147E-16	5
distance from sphere 2 to liquid level	0.15	0.005	m	5.4046E-08	2.9210E-15	5
distance from the solid to liquid level	0.30	0.005	m	-2.60912E-08	6.8075E-16	5
	0.7684942	g/cm3			6.61E-07	387
Volume of the sphere under test						
mass of weights 1	1002.714917	0.00002715	g	3.53726E-05	1.2512E-09	100
mass of weights 2	695.7230962	0.00007065	g	-9.20469E-05	8.4726E-09	100
volume of weights 1	127.6221	0.0112	cm3	-1.38762E-05	1.9255E-10	100
volume of weights 2	87.4713	0.0712	cm3	8.86244E-05	7.8543E-09	100
volume thermal expansion coefficient of the weights 1	4.80E-05	4.80E-07	/ºC	5.76296E-08	3.3212E-15	22
volume thermal expansion coefficient of the weights 2	4.80E-05	4.80E-07	/ºC	-1.47688E-07	2.1812E-14	22
air density	0.000950854	7.34266E-07	g/cm3	0.000344169	1.1845E-07	59
liquid density	0.7684942	6.60694E-07	g/cm3	0.000344246	1.1851E-07	387
air temperature	21.95	0.20	ºC	6.82081E-07	4.6523E-13	100
liquid temperature	20.043	0.0060	ºC	2.31281E-05	5.3491E-10	100
pressure over the sphere under test	83489.64	100	Pa	5.40289E-07	2.9191E-13	100
mass difference in air	5.51E-05	4.42588E-05	g	5.7663E-05	3.3250E-09	59
mass difference in liquid	4.93E-06	7.34875E-05	g	-9.57437E-05	9.1669E-09	59
volume thermal expansion coefficient of the sphere under test	9.60E-06	9.60E-08	/ºC	1.56035E-06	2.4347E-12	22
compressibility coefficient of the sphere under test	1.35E-11	1.35E-13	/Pa	-5.47448E-06	2.9970E-11	22
gravity correction for air measument	2.43922E-06	2.43E-08	g	-3.16349E-08	1.0008E-15	22
gravity correction for liquid measument	-0.000322111	3.21E-06	g	4.17754E-06	1.7452E-11	22
Volume of the sphere under test	399.91725 cm3				0.00052	187

Now in order to validate this evaluation of the volume and its uncertainty of the solid under test, values obtained from a estimation from Monte Carlo's method are presented next.

Considering for this exercise all input quantities with frequency of normal distribution (it could be used other frequency distribution for some input quantities with similar results) with mean and standard uncertainty equal to the values reported in table 1, one thousand random values for each input quantity were generated and the same number of volume values were obtained from them.

The mean and the standard deviation from the random numbers generated for each input quantity were compared with the values reported in table 1, and all them match good enough.

The mean and the standard deviation of the volume values are the next (Monte Carlo's method),

$$V'_T = 399{,}917\ 23 \pm 0{,}000\ 52\ \text{cm}^3\ (k=1)$$

frequency distribution is shown in Fig. 3. The value of volume evaluated by Monte Carlo's method is different to the evaluation with the original data in $2\text{x}10^{-5}$ cm^3 and uncertainty values are equals.

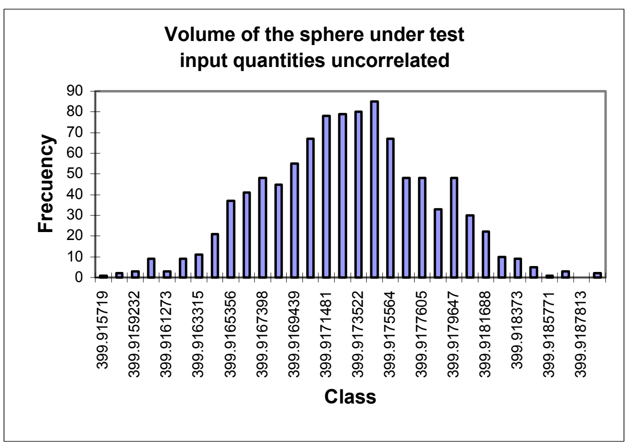

Fig. 3. Histogram of the volume values obtained from Monte Carlo Method. All input quantities uncorrelated.

It could be noted in table 1, that the uncertainty value obtained from (6) for the liquid density at the level of the sphere under test is small than uncertainties of liquid density at both top and bottom, this uncertainty value is less than the expected value.

Taking into account a component due to a correlation (correlation factor = 1) between liquid density values of top and bottom in the uncertainty evaluation of the liquid at the level of the unknown sphere using (7), [1]

$$corr_{\rho L1-\rho L2} = 2\frac{\partial \rho_{LT}}{\partial \rho_{L1}}\frac{\partial \rho_{LT}}{\partial \rho_{L2}}u_{\rho L1}u_{\rho L2}r(\rho_{L1},\rho_{L2}) \qquad (7)$$

$$corr_{\rho L1-\rho L2} = 4{,}316\text{x}10^{-13}\ \text{g}^2/\text{cm}^6$$

This value combined with the rest of components throws next value for the uncertainty of the liquid density at the level of the sphere under test,

$$u(\rho_{LT}) = \pm\ 9{,}32\text{x}10^{-7}\ \text{g/cm}^3$$

This new value is still less than the uncertainty value of one of the liquid densities measured, but the difference is quite small.

The combined standard uncertainty of the volume of the sphere under test using this new value of the liquid density at level of the solid is,

$$u\ (V_T) = \pm\ 0{,}000\ 62\ \text{cm}^3\ (k=1)$$

This value of uncertainty is approximately 16 % bigger than the uncertainty value evaluated with input quantities uncorrelated.

In order to validate this uncertainty value based in input quantities where two of them have a correlation factor by Monte Carlo's method, $r(\rho_{L1},\rho_{L2}) = 1$, it were used the same values for the last numerical analysis but now, the values of liquid density 2 were evaluated as function of the values of liquid density 1 as,

$$\rho_{L2} = \rho_{L1} + a0$$

where *a0* is a difference of liquid density, and this difference was evaluated from the mean values of ρ_{L1} and ρ_{L2}. This liquid difference was used by this way, because the density of the liquid at the bottom is always greater than in the top of the vessel due to the physical relation ship due to a combination of gradients of pressure and temperature in the column of liquid, and it could be considered stable enough for the measurement period.

The mean and the standard deviation of the volume values evaluated by this numerical method are the next,

$$V'_T = 399{,}917\ 22 \pm 0{,}000\ 62\ \text{cm}^3\ (k=1)$$

frequency distribution is shown in Fig. 4. The value of volume evaluated by Monte Carlo's method is different to the evaluation with the original data in $3\text{x}10^{-5}$ cm^3 and uncertainty value is the same that the value evaluated by GUM's method.

The small difference between the results from numerical analysis against the result from the evaluation using the mean values and formulas could arises because mean of the random numbers generated by software of the input quantities differs from its mean value in almost the same proportion.

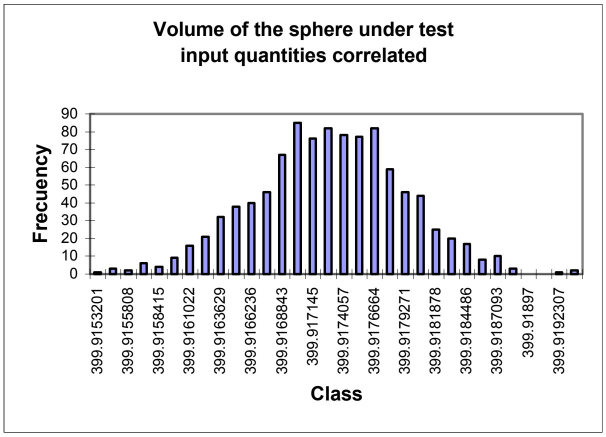

Fig. 4. Histogram of the volume values obtained from Monte Carlo Method. Taking account a correlation between two input quantities.

There is a previous value certificated for the volume of the sphere under test. The result of the measurement was compared against this value using the normalized error criteria [2] in order to check it. The value of the normalized error (for approx. 95 % level of confidence) is less than one, the difference between the values is less than the combined uncertainty of the difference (error).

6. CORRELATION BETWEEN ρ_{L1} and ρ_{L2}

For this measurement, there is a correlation between the liquid density determinations at both top and bottom, this correlation is a product to a physical relation, because it could be considered a liquid density determination for a same liquid at two levels with different instruments (solid density standard, balance, sensors, etc) and avoid all possible source of dependence in the measurement, but the physical relation ship it could not be avoid it.

For this uncertainty estimation, it is necessary to introduce a contribution due to the correlation mentioned about, because it is not usual to have an uncertainty value for a measurand determination small than the uncertainty of the input quantities.

7. CONCLUSIONS

The value of volume obtained from the measurement is consistent with the previous value (certificated value) between the uncertainty limits. The measurement procedure, the evaluation of the volume and its uncertainty seems ok.

The shapes of the frequency distributions of the volume evaluated by Monte Carlo's Method seems approximately as normal distributions, and the confidence intervals could be taken from the t distribution, but, for the evaluation of the expanded uncertainty, there is a problem with the evaluation the effective degrees of freedom for measurement models with input quantities correlated.

There is a correlation between input quantities and this correlation should been taken account for the volume uncertainty evaluation.

It is not possible to evaluate the effective degrees of freedom with correlated input quantities, and considering only the uncertainty of the liquid density at level of the solid, the contribution due to the correlation is large compared with rest of contributions, and the evaluation of effective degrees of freedom is not realistic in this case.

The correlations in measurements could have origin in metrological dependence or in physical relation ships, and both may affect the evaluation of the uncertainty.

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