Comparison of Results of the Volume Determination of Mass Standards by Weighings in Air and Conventional Hydrostatic Weighing Method

Jorge Nava-Martínez, Luis M. Peña-Pérez
Centro Nacional de Metrología, CENAM
km 4,5 Carretera a Los Cués, El Marqués, Querétaro, México.
Tel: (+52) 442 2 11 05 00, Fax: (+52) 442 2 11 05 68, e-mail: jnava@cenam.mx, lpena@cenam.mx

Abstract

Two methods for the volume determination of mass standards are compared. The conventional hydrostatic weighing method where the mass standards are immersed in water and weighings in air where the mass standards are subjected to a variation in air density of ± 10 % or less. The balance is installed in an air-tight chamber. Two kilograms were used and uncertainty analysis is compared.

1. Introduction

The kilogram is the last of the base units of the International System (SI) to be defined by an artifact [1]: The kilogram is the unit of mass: it is equal to the mass of the international prototype of the kilogram.

Since 1892 Mexico obtained the k21 the official copy of the international prototype of the kilogram and recently (2005) has obtained the k90 new copy. With these two prototypes CENAM (National Measurement Institute of Mexico) assures the mass national traceability.

However, the first link in the chain of traceability starts with the transfer of accuracy between the platinum-iridium prototype (k21 and k90) to the stainless steel reference standards, and in this case a significant buoyancy correction has to be applied to a measured apparent mass difference.

The density of the platinum-iridium is about 21 530 kgm^{-3} and the stainless steel is about 8 000 kgm^{-3} and whether the average of the air density at CENAM is 0,956 0 kgm^{-3}, it produces a correction about 75 mg and whether the mass comparator reaches a standard deviation of 2 μg, the major contribution to the uncertainty in mass is the buoyancy correction.

Normally, the well known CIPM-81/91[2] air density formula is applied to the buoyancy correction; it has an uncertainty of about 1 part in 10^4, giving a total uncertainty in air density in the best case of 1,1 parts in 10^4. With this restrain, the uncertainty due to the buoyancy correction in the comparison between platinum-iridium (density about 21 530 kgm^{-3}) against stainless steel (density about 8 000 kgm^{-3}) is of order 10 μg (at 1 kg level).

The best capability at the density lab of CENAM for the volume determination in a 1 kg weight is 2 part in 10^5 using the conventional hydrostatic method, the disadvantages of this method are: the weight is immersed in water so that an instability of mass is presented although it is not likely to cause significant corrosion [3,4], the water may cause some changes in its surface, such as, absorbed contaminants or surface oxide layer, that means the mass of the weight must be monitored in the time or checked the mass history.

The weighings in air-air method have the advantage that the problems mentioned above do not have it, however, for the application of this method the mass laboratory must have an air-tight chamber where the air volume inside may regulated and therefore the air density changed.

2. Comparisons of methods

2.1 A brief description of a conventional hydrostatic method.

The hydrostatic technique (the most accurate method mentioned in the OIML R111-2004[5]) consists in comparing the test weight both in air and a liquid of known density. The air densities in the weighings in air and water are different, so that, the measurements of air temperature, humidity and barometric pressure must be done and for water density measurements just water temperature and air pressure must be done.

The volume of two mass standards (solids weights) was obtained by the conventional hydrostatic weighing method, using pure water as transfer standard. The procedure for this method consists in weighing the solid weight immersed in two different fluids -air and pure water in this case-. Knowing the density of the two fluids is possible to obtain the volume of the solid, by means of Archimedes' principle. The mass of the solid immersed in air and in pure water was obtained by comparison with mass standards, using a weighing instrument. Figure 1 shows the system used for conventional hydrostatic weighing.

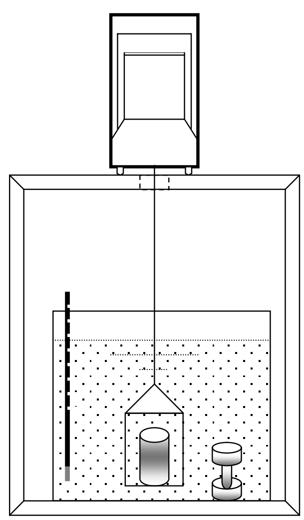


Figure 1. Hydrostatic weighing system used for the volume determination.

The mathematical model is:

$$v_x = \frac{m_{p1} - m_{p2} + \Delta m_1 - \Delta m_2 + \rho_a \left(v_{p2} Y_2 - v_{p1} Y_1 \right)}{\rho_w Z_1 - \rho_a Z_2} \tag{1}$$

where:

v_x is the volume of the unknown solid weight.
m_{p1} is the mass standard used in the weighing in air.
m_{p2} is the mass standard used in the weighing in pure water.
Δm_1 is the mass difference between the solid and the mass standard during the weighing in air.
Δm_2 is the mass difference between the solid and the mass standard during the weighing in pure water.
ρ_a is the density of air.
ρ_w is the density of pure water.
v_{p1} is the volume of the mass standard used in the weighing in air.
v_{p2} is the volume of the mass standard used in the weighing in pure water.

The factors Y_1, Y_2, Z_1 and Z_2 are the corrections for the volumetric expansion due to temperature during the weighings in air and in pure water:

$$Y_1 = 1 + \alpha_{p1}(t_a - 20) \tag{2}$$
$$Y_2 = 1 + \alpha_{p2}(t_a - 20) \tag{3}$$
$$Z_1 = 1 + \alpha_x(t_w - 20) \tag{4}$$
$$Z_2 = 1 + \alpha_x(t_a - 20) \tag{5}$$

where:

α_{p1} is the thermal volumetric expansion coefficient of the mass standard used during the weighing in air.
α_{p2} is the thermal volumetric expansion coefficient of the mass standard used during the weighing in pure water.
α_x is the thermal volumetric expansion coefficient of the solid weight.
t_a is the temperature of air.
t_w is the temperature of pure water.

The environmental conditions of the volume determination by hydrostatic weighing (temperature of air, barometric pressure, relative humidity, temperature of water) were measured with the following instruments:

- Thermohygrometer Vaisala HIM38, resolution: 0,01 ºC, U ± 0,02 ºC.
- Barometer Mensor, resolution: 1 Pa, U ± 10 Pa.
- Thermometer Kessler, resolution: 0,1 ºC, U ± 0,2 ºC.

The weighing instrument employed was a Mettler AX504, with resolution of 0,1 mg. The mass standards used were from 1 mg to 1 kg set of weights Sartorius, class E_2 [5].

The air density was calculated using the CIPM-81/91 air density formula [2].

The pure water employed in this exercise is produced at CENAM. The density of this pure water was calculated according to Tanaka et al [6] formula. These values have been confirmed by Centeno, L.M et al [7] approach.

The volume values of the solid weights with their combined standard uncertainty are:

$$\boldsymbol{V_{x1} = 126{,}735\ 7\ cm^3 \pm 0{,}001\ 5\ cm^3}$$
$$\boldsymbol{V_{x2} = 126{,}580\ 8\ cm^3 \pm 0{,}001\ 5\ cm^3}$$

Where V_{x1} is the solid weight with cylindrical shape and V_{x2} is the solid weight with bobbin shape.

2.2 The weighings in air-air method was carried out at CENAM in the national mass laboratory which is located in a basement and the air conditions are controlled. The next figure 2. shows the air-tight chamber where the Mettler HK 1 000 MC mass comparator is installed.

Figure 2. The air-tight chamber, the HK 1 000 MC mass comparator is installed inside

These measurements were carried out using the same principle described in **2.1** as follows:

If two mass standards are compared (m_R reference mass and m_x unknown mass and volumes, V_R and V_x, respectively) in air with density ρ_a, and the apparent mass difference Δm yield

$$m_x - m_R + \rho_{a1}\left(V_R - V_x\right) = \Delta m_1 \qquad (6)$$

2.2.1 The air density ρ_{a1}, is calculated at 81 000 Pa and therefore Δm_1 is obtained, this air pressure is the mean value at CENAM's level (1 820 m over the sea level).

2.2.2 The air pressure is increased inside the air-tight chamber using clean air until 88 000 Pa, the air density was changed about $\Delta\rho_a$=10%, it produces the second equation,

$$m_x - m_R + \rho_{a2}\left(V_R - V_x\right) = \Delta m_2 \qquad (7)$$

Therefore, solving the above equations (6) and (7) for the unknown volume V_x yields:

$$V_x = V_R + \frac{\left(\Delta m_2 - \Delta m_1\right)}{\left(\rho_{a1} - \rho_{a2}\right)} \qquad (8)$$

The equation (8) shows that the unknown volume does not depend of the mass.

As is described above the mass measurements were carried out in the Mettler HK 1 000 MC mass comparator, this apparatus is equipped with a carrousel with four positions and is operated under computer control, allowing up to four mass standards to be compared at one time. The standard deviation obtained during the repetition typically was 2 µg or better.

Two reference weights and two unknown weights were introduced in the scheme, one of the reference weight plays as check standard. The purpose of the reference standards is to check the buoyancy effects and monitoring the mass stability during the time of the measurements.

The matrix representation of the equation (6) of the comparison scheme of the four weights is as follows:

$$Xm + CV = Y + \varepsilon \qquad (9)$$

where *m* are the unknown mass values (the *parameters*), *Y* (the *observations*) are the mass differences observed on the balance between the weights involved in the comparison selected in the *X* matrix (the *matrix design*), *C* the *coefficients matrix* and *V* are the unknown volume values and ε is the unknown observation errors. The -1, +1 and 0 is depending of the role in the design matrix (-1 is for standard and +1 is for unknown and 0 is not included in the weighing comparison).

The equation (6) is represented as similar form of equation (9) including the all parameters involved

$$\begin{array}{c} \begin{matrix} R & x1 & x2 & x3 \end{matrix} \\ \begin{pmatrix} -1 & 1 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & 1 & 0 \\ 0 & -1 & 0 & 1 \\ 0 & 0 & -1 & 1 \end{pmatrix} \end{array} \begin{pmatrix} m_R \\ m_{x1} \\ m_{x2} \\ m_{x3} \end{pmatrix} + \begin{pmatrix} \rho_{a11} & -\rho_{a11} & 0 & 0 \\ \rho_{a12} & 0 & -\rho_{a12} & 0 \\ \rho_{a13} & 0 & 0 & -\rho_{a13} \\ 0 & \rho_{a14} & -\rho_{a14} & 0 \\ 0 & \rho_{a15} & -\rho_{a15} & 0 \\ 0 & 0 & \rho_{a16} & -\rho_{a16} \end{pmatrix} \begin{pmatrix} V_R \\ V_{x1} \\ V_{x2} \\ V_{x3} \end{pmatrix} = \begin{pmatrix} \Delta m_{11} \\ \Delta m_{12} \\ \Delta m_{13} \\ \Delta m_{14} \\ \Delta m_{15} \\ \Delta m_{16} \end{pmatrix} \text{ at 81 000 Pa} \qquad (10)$$

Where, *R* is the reference weight and *x*1, *x*2 and *x*3 are the unknown weights respectively.

The second measurements were carried out at 88 000 Pa yielding the following equation (11):

$$\begin{pmatrix} R & x1 & x2 & x3 \\ -1 & 1 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & 1 & 0 \\ 0 & -1 & 0 & 1 \\ 0 & 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} m_R \\ m_{x1} \\ m_{x2} \\ m_{x3} \end{pmatrix} + \begin{pmatrix} \rho_{a21} & -\rho_{a21} & 0 & 0 \\ \rho_{a22} & 0 & -\rho_{a22} & 0 \\ \rho_{a23} & 0 & 0 & -\rho_{a23} \\ 0 & \rho_{a24} & -\rho_{a24} & 0 \\ 0 & \rho_{a25} & -\rho_{a25} & 0 \\ 0 & 0 & \rho_{a26} & -\rho_{a26} \end{pmatrix} \begin{pmatrix} V_R \\ V_{x1} \\ V_{x2} \\ V_{x3} \end{pmatrix} = \begin{pmatrix} \Delta m_{21} \\ \Delta m_{22} \\ \Delta m_{23} \\ \Delta m_{24} \\ \Delta m_{25} \\ \Delta m_{26} \end{pmatrix} \text{ at 88 000 Pa} \qquad (11)$$

If the equation (10) is subtracted from the equation (11), the standard value is sent to right side of the equation and V_{x1} (standard) is introduced as a restraint yields:

$$\begin{pmatrix} 0 & (\rho_{a21}-\rho_{a11}) & 0 & 0 \\ 0 & 0 & (\rho_{a22}-\rho_{a12}) & 0 \\ 0 & 0 & 0 & (\rho_{a23}-\rho_{a13}) \\ 0 & (\rho_{a14}-\rho_{a24}) & (\rho_{a24}-\rho_{a14}) & 0 \\ 0 & (\rho_{ai5}-\rho_{a25}) & 0 & (\rho_{a25}-\rho_{a15}) \\ 0 & 0 & (\rho_{a16}-\rho_{26}) & (\rho_{a26}-\rho_{a16}) \\ 1 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} V_R \\ V_{x1} \\ V_{x2} \\ V_{x3} \end{pmatrix} = \begin{pmatrix} (\rho_{a21}-\rho_{a11})V_{x1} + \Delta m_{11} - \Delta m_{21} \\ (\rho_{a22}-\rho_{a12})V_{x1} + \Delta m_{12} - \Delta m_{22} \\ (\rho_{a23}-\rho_{a13})V_{x1} + \Delta m_{13} - \Delta m_{23} \\ \Delta m_{14} - \Delta m_{24} \\ \Delta m_{15} - \Delta m_{25} \\ \Delta m_{16} - \Delta m_{26} \\ V_R \end{pmatrix} \qquad (12)$$

Using the Gauss Markov Estimator [8,9] for the solution of the equation (12), the unknown volumes are estimated as follows:

$$\beta_{GM} = \left(X^T \Phi^{-1} X\right)^{-1} X^T \Phi^{-1} Y \qquad (13)$$

Where Φ^{-1} is minimum variance matrix according with the GM approach [8], and it is the combined standard uncertainty according with the ISO Guide [10].

Similar approach was presented by Becerra L.O. et al [9] where the volume and mass of the weights are determined simultaneously, the hydrostatic conventional method for this approach is used and the example is for the kilogram subdivision.

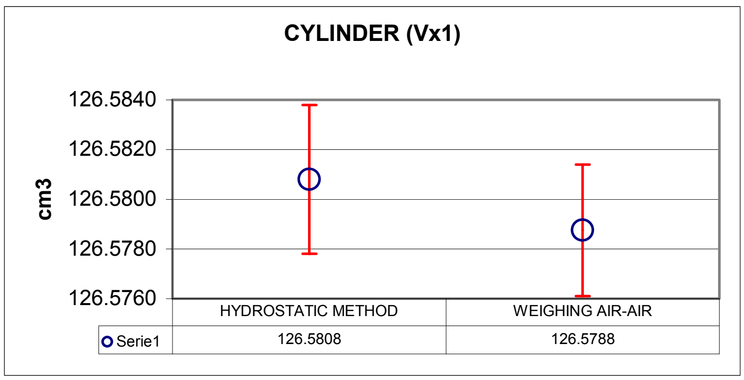
3. The mass standards

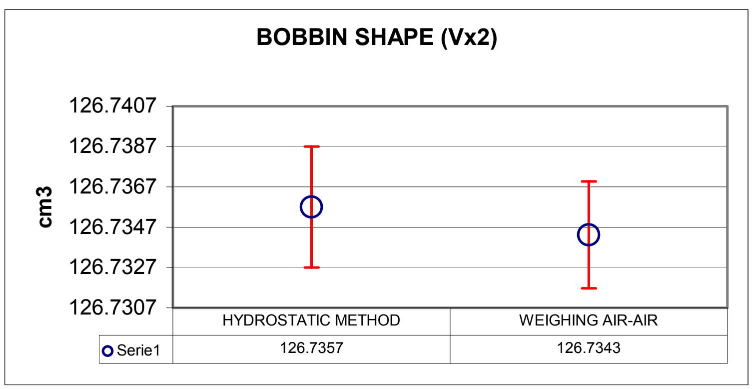
Four mass standards were used for this approach all of them are of stainless steel, one was the reference standard and other check standard (Häfner E_1 weights) and the last two were as unknown weights and were manufactured at CENAM since 1999 with quality of the material and their surface finish equivalent to that for mass standards of the class OIML Class E_2[5]. These were identified as cylinder shape and Bobbin shape.

4. Measurements

The measurements were carried using the hydrostatic conventional method from 27 to 31 of March after the appropriated thermal stabilization time (one and half week) the second measurements air-air method were carried out from 11 to 26 April.

The comparative final results are showed in the following graphics 1and 2.





In order to know the degree of equivalence between the two methods, the E_n [11] value is applied and the result is the following:

Weight	E_n-value
Cylinder (Vx1)	0,5
Bobbin Shape (Vx2)	0,3

5. Conclusions

The results show that the two methods agree on the solid weights used, these are well within the combined uncertainty of the measurements also the results demonstrate that the second method (weighings air-air) is capable of making high-accuracy measurements of the volume.

The advantage of the proposed method (air-air method) for volume determination is that the mass standards remain in position on the weight chamber during the measurements.

The mass instability due to the immersing into the water of the weight is avoided, although, the appropriate stabilization time is taken into account.

The air-tight chamber has to keep the air density almost in a variation of 0,000 2 kgm^{-3}.

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