Uncertainty of factor *Z* in gravimetric volume measurement

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ABSTRACT
In the gravimetric volume measurement method, the factor *Z* is generally used to facilitate an easy conversion from the apparent mass obtained using a balance to the liquid volume. The uncertainty of the measurement used for the liquid volume can be divided into two specific contributions: one from the components related to the mass measurements and one from those related to the mass-to-volume conversion. However, some ISO standards and calibration guides have suggested that the uncertainty due to the factor *Z* is generally neglected in the uncertainty calculation pertaining to gravimetric volume measurement. This paper describes the combined effects of the density of the water, the density of the reference weights, and the air buoyancy on the uncertainty of factor *Z* in terms of how they subsequently affect the uncertainty of the measurement results.

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1. INTRODUCTION

The ISO 4787 standard describes the general equation for the calculation of the volume at the reference temperature of 20 °C, V_{20}, from the apparent mass of the water, be it contained or delivered, as follows from [1], B.1:

$$V_{20} = (I_L - I_E) \left(\frac{1}{\rho_W - \rho_A} \right) \left(1 - \frac{\rho_A}{\rho_B} \right) [1 - \gamma(t - 20)] \,, \qquad (1)$$

where I_L is the balance reading of the vessel containing water (g), I_E is the balance reading of empty vessel (g), ρ_W is the density (g/mL) of the water at temperature t, ρ_A is the density of air (g/mL), ρ_B is the actual density of the reference weights (8 g/mL), γ is the coefficient of the cubic thermal expansion of the material (°C^{-1}), and t is the temperature of the water used in the testing (°C).

Since this equation is somewhat complicated to work with, the factor *Z* is provided to simplify the volume calculation:

$$V_{20} = m Z [1 - \gamma(t - 20)] \,, \qquad (2)$$

where m is the net weighed values of $I_L - I_E$ and Z is the conversion factor of the mass of the water measured in terms of volume at the measurement temperature.

2. DETERMINATION OF FACTOR Z

The factor *Z* depends on the air density, water density, water temperature, and the density of the reference weights. The factor can be derived from (1) as follows:

$$Z = \left(\frac{1}{\rho_W - \rho_A} \right) \left(1 - \frac{\rho_A}{\rho_B} \right). \qquad (3)$$

To determine the value of factor *Z*, the following parameters must be taken into account:

- density of air ρ_A in relation to atmospheric pressure, temperature and a relative humidity of 40 % – 90 %;
- density of water ρ_W in relation to temperature;
- density of the reference weights ρ_B of the balance used.

2.1. Determining the air density

The air density ρ_A in kg m^{-3} can be determined with sufficient uncertainty from the following CIPM approximation formula for air density [2], E.3-1:

$$\rho_A = \frac{0.348\,48\,P - 0.009\,hr \times e^{0.061 \times t}}{273.15 + t} \,, \qquad (4)$$

where P is the atmospheric pressure (hPa), hr is the relative humidity (%), and t is the atmospheric temperature (°C).

Table 1. Air density values as a function of temperature at 1,013.25 hPa and a 50 % relative humidity.

Temperature in °C	Density of air in g/mL
15	0.001 225
20	0.001 204
25	0.001 184

Table 1 presents the air density to temperature relationship at 1,013.25 hPa and a 50 % relative humidity.

2.2 Determining the water density

The density of air-free water ρ_W' at a pressure of 1,013.25 hPa and a temperature t between 0 °C and 40 °C expressed in terms of the ITS-90 is given by Tanaka et al. [3] as follows:

$$\rho_W' = a_5 \left[1 - \frac{(t + a_1)^2 (t + a_2)}{a_3 (t + a_4)} \right], \tag{5}$$

where

$a_1 = (-3.983\ 035 \pm 0.000\ 67)\ °C$

$a_2 = 301.797\ °C$

$a_3 = 522\ 528.9\ °C^2$

$a_4 = 69.348\ 81\ °C$

$a_5 = (0.999\ 974\ 950 \pm 0.000\ 000\ 84)\ g/mL$

$t = $ water temperature in $°C$.

Since the pure water that is used in the laboratory is generally air-saturated, the density must be corrected. To adjust the air-free water density as described in (5) to air-saturated water between 0 °C and 25 °C (the standard laboratory condition), we can use the following [3], 5.2:

$$\Delta\rho = s_0 + s_1 \times t, \tag{6}$$

where

$$\frac{s_0}{kg\ m^{-3}} = -4.612 \times 10^{-3}$$

$$\frac{s_1}{kg\ m^{-3}\ °C^{-1}} = 0.106 \times 10^{-3}.$$

Moreover, since water is slightly compressible, a small correction may be required under typical laboratory conditions.

The compressibility factor F_c [3], 5.3, for the water density used at different pressures is as follows:

$$F_c = 1 + [(k_0 + k_1 t + k_2 t^2) \Delta P], \tag{7}$$

where

$\Delta P = P - (101\ 325\ Pa)$

$k_0 = 50.74 \times 10^{-11}\ Pa^{-1}$

$k_1 = -0.326 \times 10^{-11}\ Pa^{-1}\ °C^{-1}$

$k_2 = 0.004\ 16 \times 10^{-11}\ Pa^{-1}\ °C^{-2}$

$$\rho_W = (\rho_W' \times F_c + \Delta\rho) \tag{8}$$

with $\rho_W = $ the density of air-saturated water and

$\rho_W' = $ the density of air-free water.

Table 2. Water density values after correction for air-saturated distilled water.

Water temperature (°C)	Air-free water density (g/mL)	Correction for air saturation (g/mL)	Air-saturated water density (g/mL)
15	0.999 102 57	- 0.000 003 02	0.999 099 55
20	0.998 206 75	- 0.000 002 49	0.998 204 25
25	0.997 047 02	- 0.000 001 96	0.997 045 06

Table 3. Air-saturated water density as a function of water temperature and pressure.

Water temperature (°C)	Air-saturated water density (g/mL) at atmospheric pressure of		
	900 hPa	1,013.25 hPa	1,050 hPa
15	0.999 094 26	0.999 099 55	0.999 101 27
20	0.998 199 07	0.998 204 25	0.998 205 94
25	0.997 039 96	0.997 045 06	0.997 046 72

Table 2 presents examples of water density as a function of water temperature for distilled water at 1,013.25 hPa after correction for any dissolved gasses in the water.

Meanwhile, Table 3 presents examples of calculated air-saturated water density as a function of water temperature and pressure after applying corrections for the dissolved gasses in the water.

2.3 Density of the reference weights

The density of the reference weights/mass pieces ρ_B that are used for the balance calibration is normally presented in the calibration certificate of the weights. Alternatively, the uncertainties corresponding to the used weight class according to OIML R 111-1 [2] can be used. If the density of the reference weights are not known, 8.0 g/mL is generally used.

2.4 Determining the factor Z values

The values of the conversion factor Z (mL/g) as a function of temperature and pressure as given in the existing literature mainly pertain to distilled water. When liquids other than distilled water are used, the correction factors (factor Z) for the specific liquid must be determined.

Table 4 presents the factor Z values in relation to temperature and pressure. The calculations were based on (3) and (8).

3. THE UNCERTAINTY OF FACTOR Z

3.1 Sources of uncertainty in factor Z

Having identified the input quantities of factor Z using (3), it is possible to determine the sources of uncertainty pertaining to the different input quantities, which are:

Table 4. Factor Z values as a function of water temperature and pressure.

Water temperature (°C)	Value of factor Z (mL/g) at atmospheric pressure of		
	900 hPa	1,013.25 hPa	1,050 hPa
15	1.001 845	1.001 958	1.001 995
20	1.002 745	1.002 858	1. 002 895
25	1.003 912	1.004 026	1.004 062
27	1.004 448	1.004 562	1.004 599

- water density
- air density
- density of the reference weights.

The uncertainty of factor Z can be determined using the GUM law of propagation of uncertainty [4] as follows:

$$u(Z) = \sqrt{\left(\frac{\partial Z}{\partial \rho_A} u(\rho_A)\right)^2 + \left(\frac{\partial Z}{\partial \rho_W} u(\rho_W)\right)^2 + \left(\frac{\partial Z}{\partial \rho_B} u(\rho_B)\right)^2} \quad (9)$$

where $u(\rho_A)$ is the standard uncertainty of the air density (g/mL), $u(\rho_W)$ is the standard uncertainty of the water density (g/mL), and $u(\rho_B)$ is the standard uncertainty of the reference weights (g/mL).

3.2 Uncertainty of air density

At a relative humidity of hr = 0.5 (50 %), a temperature of 20 °C and a pressure of 1,013.25 hPa, the uncertainty of the air density can be estimated according to OIML R111 [2], C.6.3-3, as follows:

$$\frac{u(\rho_A)}{\rho_A} = \sqrt{\begin{array}{l}(1 \times 10^{-4})^2 + (-3.4 \times 10^{-3} \times u(t))^2 \\ + (1 \times 10^{-3} \times u(P))^2 + (-10^{-2} \times u(hr))^2\end{array}}, \quad (10)$$

where $u(t)$ is the uncertainty of the air temperature t (°C), $u(P)$ is the uncertainty of the air pressure P (hPa), and $u(hr)$ is the uncertainty of the relative humidity hr (%).

For the uncertainty values ($k = 2$) from the calibration of the pressure, temperature and humidity sensors, the uncertainty due to the temperature of the air is 0.1 °C, the uncertainty due to the barometric pressure is 0.1 hPa, and the uncertainty due to the relative humidity is 1 %. This yields the following:

$$u(\rho_A) = 0.0012 \text{ g/mL}$$

$$\times \sqrt{\begin{array}{l}(1 \times 10^{-4})^2 + \left(-3.4 \times 10^{-3} \times \frac{0.1}{2}\right)^2 \\ + \left(1 \times 10^{-3} \times \frac{0.1}{2}\right)^2 + \left(-1 \times 10^{-2} \times \frac{0.01}{2}\right)^2\end{array}}$$

$$= 2.52 \times 10^{-7} \text{ g/mL}.$$

3.3 Uncertainty of water density

The uncertainty of the water density can be evaluated from the formulation given by EURAMET cg 19 [5], 7.3.3, as follows:

$$u(\rho_W) = \sqrt{u^2(\rho_{W,F}) + u^2(\rho_{W,t}) + u^2(\delta\rho_W)}, \quad (11)$$

where

$$u(\rho_{W,t}) = u(t_W) \times \beta \times \rho_W(t_W)$$

$$u(t_W) = \left[\left(\frac{U(\text{ther})}{k}\right)^2 + u(\text{res})^2\right]^{0.5}$$

$$u(t_W) = \left[\left(\frac{0.01 \text{ °C}}{2}\right)^2 + \left(\frac{0.01 \text{ °C}}{2\sqrt{3}}\right)^2\right]^{0.5}$$

$$u(t_W) = 0.006 \text{ °C}.$$

The expansion coefficient can be estimated as follows:

$$\beta = (-0.117\,6\,t^2 + 15.846\,t - 62.677) \times 10^{-6} \text{ °C}^{-1}$$

$$\beta = (-0.117\,6 \times 20^2 + 15.846 \times 20 - 62.677) \times 10^{-6} \text{ °C}^{-1}$$

$$\beta = 0.000\,21 \text{ °C}^{-1}$$

$$\rho_W(t_W) = 0.998\,204\,25 \text{ g/mL (from Table 3)}$$

$$u(\rho_{W,t}) = 0.006 \times 0.000\,21 \times 0.998\,204\,25$$

$$u(\rho_{W,t}) = 1.26 \times 10^{-6} \text{g/mL} \sim 1 \times 10^{-6} \text{g/mL}.$$

The standard uncertainty related to $u(\delta\rho_W)$ could range from a few ppm for highly pure water (measured by means of a high-resolution density meter) to 10 ppm for distilled or de-ionised water, provided that the conductivity is less than 5 µS/cm, meaning it is assumed to be 5×10^{-6} g/mL.

Meanwhile, $u(\rho_{W,F})$ is the estimated standard uncertainty of the formulation (4.5×10^{-7} g/mL), $u(\rho_{W,t})$ is the uncertainty due to the temperature of the water (1×10^{-6} g/mL), and $u(\delta\rho_W)$ is the uncertainty due to the purity of the water (5×10^{-6} g/mL) [5], 8.2.3. This yields the following:

$$u(\rho_W) = \sqrt{(4.5 \times 10^{-7})^2 + (1 \times 10^{-6})^2 + (5 \times 10^{-6})^2} \text{ g/mL}$$

$$= 5.12 \times 10^{-6} \text{ g/mL}. \quad (12)$$

3.4 Uncertainty of the reference weights

The uncertainty of the density of the weights/mass pieces is presented in the calibration certificate of the weights, or alternatively, according to OIML R111-1, the uncertainty of stainless-steel weights Class E2 is 140 kg/m³ ($k = 2$).

The uncertainty of the density of the reference weights is normally presented in the calibration certificate of the weights. For example, the value presented in the calibration certificate of the set of weights used is 0.06 g/mL ($k = 2$):

$$u(\rho_B) = \frac{\rho_r}{2} = \frac{0.06}{2} \text{ g/mL} = 0.03 \text{ g/mL}. \quad (13)$$

Alternatively, the uncertainty of the density of the weights, as presented in OIML R111-1, can also be used.

3.5 Calculating the uncertainty of factor Z

Table 5 presents example data for the calculation of the uncertainty of factor Z for air-saturated distilled water at a temperature of 20 °C and a barometric pressure of 1,013.25 hPa.

Sensitivity Coefficient of Air Density

$$\frac{\partial Z}{\partial \rho_A} = \left(\frac{1}{\rho_W - \rho_A}\right)\left(-\frac{1}{\rho_B}\right) + \left(1 - \frac{\rho_A}{\rho_B}\right)\left(\frac{1}{(\rho_W - \rho_A)^2}\right)$$

$$= 0.880\,500 \text{ mL}^2/\text{g}^2$$

Sensitivity Coefficient of Water Density

$$\frac{\partial Z}{\partial \rho_W} = \left(1 - \frac{\rho_A}{\rho_B}\right)\left(\frac{-1}{(\rho_W - \rho_A)^2}\right) = -1.005\,876 \text{ mL}^2/\text{g}^2$$

Sensitivity Coefficient of Density of Reference Weights

$$\frac{\partial Z}{\partial \rho_B} = \left(\frac{1}{\rho_W - \rho_A}\right)\left(\frac{\rho_A}{\rho_B^2}\right) = 1.887\,6 \times 10^{-5} \text{ mL}^2/\text{g}^2$$

Table 5. Example data.

Parameter	Value	Uncertainty ($k = 1$)
Air density	0.001 204 g/mL	2.52×10^{-7} g/mL
Water density	0.998 204 g/mL	5.12×10^{-6} g/mL
Mass density	8.0 g/mL	0.03 g/mL
Factor Z	1.002 858 mL/g	(Refer to the conditions in Table 4)

Uncertainty of Factor Z ($k = 1$)

$$u(Z) = \sqrt{\left(\frac{\partial Z}{\partial \rho_A}u(\rho_A)\right)^2 + \left(\frac{\partial Z}{\partial \rho_W}u(\rho_W)\right)^2 + \left(\frac{\partial Z}{\partial \rho_B}u(\rho_B)\right)^2}$$

$$= \sqrt{\begin{array}{l}(0.880\,500 \times 2.52 \times 10^{-7})^2 \\ +(-1.005\,876 \times 5.12 \times 10^{-6})^2 \\ +(1.887\,6 \times 10^{-5} \times 0.03)^2\end{array}} \text{ mL/g}$$

$$= 5.2 \times 10^{-6} \text{ mL/g}.$$

4. DISCUSSION

As shown in Table 4, the factor Z variation in distilled water due to water temperature is approximately 2.0×10^{-3} mL/g or 2.0×10^{-4} mL/(g °C) between 15 °C and 25 °C. This implies that when the uncertainty of the temperature measurement of distilled water is 0.1 °C, this will present an uncertainty of approximately 0.002 % following the conversion to volume. Meanwhile, the influence of barometric pressure on the factor Z is approximately 1×10^{-4} mL/g or 0.01 % per pressure change of 100 hPa between 900 hPa and 1,050 hPa. The uncertainty of the pressure measurement in the laboratory is typically 5 hPa. This will cause the uncertainty to the conversion of volume by less than 0.000 5 %.

5. CONCLUSIONS

The factor Z does not only depend on the density of the liquid compensated for water temperature and pressure but also on the air density and the density of the weights used for the calibration of the balance. However, the contribution to the evaluation of uncertainty resulting from the factor Z for gravimetric volume measurement is extremely small compared to that resulting from the operator process (i.e., meniscus reading) [5], 8.2.7, and the mass of water determination, provided that the measuring instruments (balance, barometer, thermometer, etc.) are used in accordance with the specifications given in the standard operating procedure (SOP). Thus, it is good practice to neglect the uncertainty of the factor Z in the evaluation of uncertainty and to give only the components related to the mass measurement process [6].

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