Guidelines on the Determination of Uncertainty in Gravimetric Volume Calibration

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Flow

Authorship and Imprint

This document was developed by the EURAMET e.V., Technical Committee for Flow. Version 4.1 was developed thanks to the cooperation of Matjaz Gaber (MIRS, Slovenia), Elsa Batista (IPQ, Portugal), Andrea Malengo, (INRIM, Italy), Ljiljana Micic (DMDM, Serbia), Tobias Nickschick (PTB, Germany), Erik Smits (VSL, Netherlands) and Olaf Schnelle-Werner (DKD, Germany). This guide builds upon the efforts of previous versions, where other authors were involved too, including Zoe Metaxiotou (EIM, Greece), Alfonso Lobo Robledo (CEM, Spain), and Umit Akcadag (UME, Türkiye).

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The document has been updated to correct typographical errors: the index of coefficient a_3 in the denominator of formula (2) has been corrected (previously shown as a_4), and the unit of measurement for coefficient a_2, located below formula (2), has been revised by removing the exponent.

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Guidelines on the Determination of Uncertainty in Gravimetric Volume Calibration

Purpose

This document has been produced to harmonise the uncertainty calculation in gravimetric determination of volume and to enhance the equivalence and mutual recognition of calibration results obtained by laboratories performing calibrations of gravimetric volume.

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1 INTRODUCTION

Liquid volume measurement is an important step in most industrial and analytical measurement operations. Volume instruments are used in many fields like chemistry, health, biology and pharmacy. In several applications within these fields the measurement of volume is significant or even critical, therefore it is important to ensure that volume quantities measured using these instruments are reliable. In order to identify and reduce possible errors in liquid handling, it is necessary to calibrate the volume instruments using the correct methods. It is also necessary to evaluate the measurement uncertainty as this information must accompany the final measurement result to give the end user confidence in the measurement.

Volume instruments can be calibrated by filling, or emptying, using a reference volume measurement, i.e. by comparing two volumes. This is a secondary method of calibration. At the highest level of the traceability chain, the volume can be determined by the primary method of weighing the quantity of a suitable liquid, contained or delivered by the volume instrument, provided that the temperature and density of the liquid are known (gravimetric method). In this guide, the evaluation of measurement uncertainty is outlined for the latter method, following the GUM [1].

Uncertainty contributions can be evaluated on the basis of statistical calculations, such as the determination of an experimental standard deviation, or the determination of the expected drift of a measurement instrument based on several previous calibrations (called “Type A” evaluation). In other cases uncertainty contributions must be evaluated on the basis of all available sources of information, and through the operator’s knowledge and expertise (called “Type B” evaluation). The criteria and formulae suggested in this Guide are not intended to, nor can they replace the personal judgment and responsible evaluation individually made by the metrologist in any particular application and laboratory.

This document contains guidance for the determination of uncertainty in gravimetric volume calibration of following volume instruments:

- Laboratory glass and plastic ware (single-volume pipettes, graduated pipettes, burettes, volumetric flasks, graduated measuring cylinders);
- Pycnometers;
- Standard capacity measure (standard test measures, proving tanks, standard flasks);
- Overflow pipettes;
- Piston-operated volumetric apparatus.

2 TERMINOLOGY AND SYMBOLS

The terminology used in this document is mainly based on existing documents:

- JCGM 100 [1] for terms related to the determination of results and uncertainty of measurement,
- JCGM 200 [2] for terms related to the calibration,
- ISO 4787 [4] for technical terms,
- ISO 8655 [13] for technical terms,
- OIML R120 [14] for technical terms.

Symbols whose meaning are not self-evident, will be explained where they are first used.

3 GRAVIMETRIC METHOD

The gravimetric method is the standard calibration method used by National Metrology Institutes (NMIs), Designated Institutes (DIs) and by accredited laboratories to calibrate volume instruments. The method consists of weighing the instrument under calibration when empty and again when full with appropriate liquid. The difference obtained in the weighing measurements gives the mass of contained or delivered liquid. Volume instruments are usually provided with reference lines or marks in order to precisely define the liquid volume. The volume adjustment with respect with those lines or marks is very important for the measurement. Also important are the draining and drying procedures of the volume instrument applied during calibration since they both affect the result. The liquid used is generally pure water (distilled, bi-distilled, or deionized) with a conductivity lower than 5 μS/cm [3] and chosen to suit the level of accuracy required relative to the amount of water used. A conversion is then performed from mass to volume at a reference temperature of t_0 (normally 20 °C). The recommended equation is described in ISO 4787 standard [4] and given below (1):

$$V_0 = \left(I_L - I_E\right) \times \frac{1}{\rho_W - \rho_A} \times \left(1 - \frac{\rho_A}{\rho_B}\right) \times \left[1 - \gamma\left(t - t_0\right)\right] \quad (1)$$

Where are:

V_0 volume, at the reference temperature t_0 , in mL

I_L weighing result (or result of the substitution, double substitution or other method of weighing) of the recipient full of liquid, in g

I_E weighing result (or result of the substitution, double substitution or other method of weighing) of the empty recipient, in g

ρ_W liquid density, in g/mL, at the calibration temperature t_W , in °C, according to equation (2)

ρ_A air density, in g/mL, according to equation (4)

ρ_B density of the reference weights used during measurement (substitution) or during calibration of the balance, assumed to be 8.0 g/mL

γ cubic thermal expansion coefficient of the material of the instrument under calibration, in °C^{-1}. (Note: the cubical expansion coefficient is normally assumed to be 3 times the linear expansion coefficient for the given material.)

t temperature of the instrument under calibration, assumed to be equal to the temperature of the liquid used in the calibration, in °C

t_0 reference temperature, in °C

Note: it can be shown that the air density to be considered is (in principle) the density of the air inside the volumetric instrument (see 5.3.4) and displaced when the instrument is filled with liquid. It is generally assumed that the ambient air density (the density of air surrounding the instrument) does not change significantly between and during both weighing. This ensures that the buoyancy effect exerted on the volumetric instrument is constant. If the ambient air density changes, the (true) mass of the instrument must be determined for each weighing as a condition for an accurate measurement of the mass of the contained liquid.

Note: Temperature of the instrument under calibration t is usually not known. Because of that it is assumed that temperature of instrument under calibration is equal to temperature of water t_W inside the instrument. This results in an additional contribution to measurement uncertainty.

The density of pure water is normally provided from formulae given in the literature. Batista and Paton [5] provide an overview of common formulae used in practice. It is, however, generally accepted that the formula given by Tanaka [6] provides a good basis for standardisation:

$$\rho_W = a_5 \left[1 - \frac{(t_W + a_1)^2 (t_W + a_2)}{a_3 (t_W + a_4)} \right] \quad (2)$$

Where are:

t_W water temperature, in °C

$a_1 = -3.983035$ °C

$a_2 = 301.797$ °C

$a_3 = 522528.9$ (°C)^2

$a_4 = 69.34881$ °C

$a_5 = 0.999974950$ g/mL

Note: a_5 is the maximum density value of SMOW water in one atmosphere (at 3.98 °C). Many users of water rely on tap water instead of SMOW. Thus a_5 must be changed accordingly to reflect the density of the water used. Also, the correction due to air content in the water can be done according to the following formula described in [6]:

$$\Delta\rho = s_0 + s_1 t_W \text{ g/mL} \quad (3)$$

Where are:

t_W water temperature, in °C

$s_0 = -4.612 \times 10^{-6}$ g/mL

$s_1 = 0.106 \times 10^{-6}$ g/mL°C

The full equation of state for water provided by the International Association for Properties of the Water Substance (IAPWS) can also be used to determine the density of the used water and a formula based on this equation is given in [5]. This provides an alternative to the Tanaka formula and should be used at temperatures above 30 °C.

Where pure water is not available, the density of the water may be determined, and the chosen formula used to determine the temperature expansion factors with insignificant loss of accuracy.

The density of the air can be determined according to several formulas described in the literature [7], [8] and [9]. For the purpose of this guide and in order to harmonize with EURAMET guide cg 18, Appendix 1, the simplified CIPM formula for the air density is used, under the constraints given below [8]:

$$\rho_A = \frac{0.34848 p_A - 0.009 h_r \exp(0.061 t_A)}{t_A + 273.15} \text{ kg/m}^3 \tag{4}$$

Where are:

t_A ambient temperature, in °C

p_A barometric pressure, in hPa

h_r relative air humidity, in %rh

Under the following conditions: barometric pressure between 600 hPa and 1100 hPa, ambient temperature between 15 °C and 27 °C and relative humidity between 20 %rh and 80 %rh, the relative uncertainty of this formula is 2.4×10^{-4}.

4 PARAMETERS THAT MAY AFFECT THE MEASUREMENT RESULT AND ITS ASSOCIATED UNCERTAINTY IN GRAVIMETRIC DETERMINATION OF VOLUME

During the gravimetric calibration of volume instruments, the main parameters that can influence the quality of the result are the following.

4.1 Weighing

Weighing is the most important step in gravimetric calibration. The weighing results are influenced by several factors such as the resolution and sensitivity of the balance, the calibration of the balance (eccentricity, linearity, and repeatability), the class and density of the reference weights used to calibrate an electronic scale or balance.

4.2 Water characteristics

Mass is converted into volume using the density of the calibration liquid. This value can be obtained from equation (2) or from the literature [5,6] or from direct measurements, if pure water is not available.

The water temperature influences the determination of the water density; thus, it should be carefully measured and recorded in each measurement. Methods for estimating the temperature of the water without affecting the volume must be established.

The viscosity of water at a specific temperature influences the residual volume in volume instruments used to deliver.

4.3 Ambient conditions

The ambient conditions (air temperature, humidity, barometric pressure) influence gravimetric measurement mainly through the air density determination, so those quantities must be measured and recorded during the measurements because of the possible fluctuations.

4.4 Volume instrument characteristics

The characteristics of the instrument (tank, volume measure, pipette, etc) under calibration, e.g. the scale or the expansion coefficient of the material, air cushion effect, must also be considered.

The volume instrument temperature depends on the ambient temperature and on the water temperature. This variation is important for the volume conversion at the reference temperature.

4.5 Other parameters

There are other parameters that can directly affect the measurements, namely the evaporation or the operator skills and experience that have a direct impact on the accuracy of the calibration result since he or she has direct influence on several steps during calibrations (e.g. meniscus reading, filling and emptying procedure or in the handling of the equipment).

5 GENERAL PROCEDURE FOR THE UNCERTAINTY CALCULATION

In this document, the evaluation of measurement uncertainty follows the methods described in the Guide to the Expression of Uncertainty in Measurement (GUM) [1]. The method consists of the following steps.

1. Expressing, in mathematical terms, the relationship between the measurand and its input quantities.
2. Determining the expectation value of each input quantity.
3. Determining the standard uncertainty of each input quantity.
4. Determining the degree of freedom for each input quantity.
5. Determining all covariance between the input quantities.
6. Calculating the expectation value for the measurand.
7. Calculating the sensitivity coefficient of each input quantity.
8. Calculating the combined standard uncertainty of the measurand.
9. Calculating the effective degrees of freedom of the combined standard uncertainty.
10. Choosing an appropriate coverage factor, k, to achieve the required confidence level.
11. Calculating the expanded uncertainty.

It should be noted that for steps 6 to 11 well suited computer programmes exist which can avoid the error-prone manual calculation. Step 1 is the most important part in the whole GUM procedure.

6 PROCEDURE FOR CALCULATING UNCERTAINTY IN GRAVIMETRIC DETERMINATION OF VOLUME

6.1 Mathematical expression of the volume V_0

$$V_0 = \frac{m}{\rho_\mathrm{W}\left(t_\mathrm{W}\right) - \rho_\mathrm{A}\left(t_\mathrm{A}, p_\mathrm{A}, h_\mathrm{r}\right)} \times \left(1 - \frac{\rho_\mathrm{A}\left(t_\mathrm{A}, p_\mathrm{A}, h_\mathrm{r}\right)}{\rho_\mathrm{B}}\right) \times \left[1 - \gamma\left(t - t_0\right)\right] + \quad (5)$$

$$+ \delta V_\mathrm{op} + \delta V_\mathrm{evap} + \delta V_\mathrm{rep}$$

With

$m = \left(I_\mathrm{L} - I_\mathrm{E}\right) + \delta m$

$t_\mathrm{W} = t_\mathrm{W0} + \delta t_\mathrm{W}$

$t_\mathrm{A} = t_\mathrm{A0} + \delta t_\mathrm{A}$

$t = t_\mathrm{W} + \delta t_\mathrm{s}$

$\rho_\mathrm{W}\left(t_\mathrm{W}\right) = \rho_\mathrm{W,form}\left(t_\mathrm{W}\right) + \delta\rho_\mathrm{W,form}$

$\rho_\mathrm{A}\left(t_\mathrm{A}, p_\mathrm{A}, h_r\right) = \rho_\mathrm{A,form}\left(t_\mathrm{A}, p_\mathrm{A}, h_\mathrm{r}\right) + \delta\rho_\mathrm{A,form}$

Where are:

- m mass contained or delivered by the volume instrument at actual conditions
- δm component arising because of influences not covered by $u\left(I_\mathrm{L}\right)$ and $u\left(I_\mathrm{E}\right)$
- $u\left(I_\mathrm{L}\right)$ uncertainty component of the weighing result of the recipient full of liquid
- $u\left(I_\mathrm{E}\right)$ uncertainty component of the weighing result of the empty recipient
- t_W0 measured water temperature
- δt_W deviation arising from lack of homogeneity in the temperature within the weighed water mass
- t_A0 measured air temperature
- δt_A deviation arising from air temperature inhomogeneity
- δt_s difference between water and artefact temperature
- $\rho_\mathrm{W,form}$ used water density formula (e.g. Tanaka's equation)

$\rho_{\text{A,form}}$ used air density formula (e.g. CIPM equation)

$\delta\rho_{\text{W,form}}$ estimated deviation from formula conditions (for water density)

$\delta\rho_{\text{A,form}}$ estimated deviation from formula conditions (for air density)

δV_{op} auxiliary quantity to consider possible errors or biases due to meniscus reading

δV_{evap} auxiliary quantity to consider possible errors or biases due to the evaporation

Note: all δx terms have usually expected value 0! They are auxiliary quantities to treat uncertainties and degrees of freedom.

n repetitions of the volume determination are performed, and an average is calculated in the following manner:

$$V_{0,\text{Average}} = \sum_{k=1}^{n} \frac{V_{0,k}}{n} \qquad (6)$$

6.2 Sources of uncertainty in volume determination

Once identified the input quantities of the measurand, i.e. the volume V , in equation (1), it is possible to identify the sources of uncertainty coming from the different input quantities, which are:

- Mass
- Temperature (water and volume instrument)
- Water density
- Air density
- Density of reference weights
- Cubic thermal expansion coefficient of the material of the instrument under calibration
- Operator effect (meniscus reading or handling of volume instrument)
- Evaporation
- Measurement repeatability
- Other sources of uncertainty of the measurement

Note: the gravimetric primary calibration of volume standards is normally performed by means of repeated, independent measurements: in this connection, it should be noted that the measurand (volume of the contained or delivered liquid) is not generally the same for repeated measurements, mainly owing to the variability of the quantity of water wetting the interior walls of the empty vessel (if it is not to be weighed in the dry state) and the variability of meniscus shape and positioning. In other words, the measurand is not perfectly reproducible for all measurements and its own variability frequently exceeds the uncertainty of each single volume determination.

6.3 Standard uncertainty of each input quantity

In the following, the different expressions of these uncertainties are displayed.

6.3.1 Mass

Equation (7) is a possible expression for this uncertainty component:

$$u(m)=\sqrt{u^2(I_\mathrm{L})+u^2(I_\mathrm{E})-2r(I_\mathrm{L},I_\mathrm{E})u(I_\mathrm{L})u(I_\mathrm{E})+u^2(\delta m)} \tag{7}$$

The measurement uncertainty of I_L and I_E should be determined according to EURAMET Calibration Guide No 18 (cg 18) [8].

Some correlations are present between the two readings of the weighing instrument (although they are obtained at different loads) as weighing instrument performance and ambient conditions do not change in a short time interval; moreover, a single set of mass standards is normally used as a reference. However, the weak covariance, expressed by a low value of the correlation coefficient $r(I_\mathrm{L},I_\mathrm{E})$, may be negligible when compared with the other uncertainty components.

The resolution (scale division) should also be considered for the uncertainty of the mass.

6.3.2 Temperature (volume instrument and water)

Equation (8) is a possible expression for this uncertainty component:

$$u(t)=\sqrt{u^2(t_\mathrm{W})+u^2(\delta t_\mathrm{s})} \tag{8}$$

And,

$$u(t_\mathrm{W})=\sqrt{\left(\frac{U(\mathrm{ther})}{\mathrm{k}}\right)^2+u^2(\mathrm{res})+u^2(\delta t)+u^2(\delta t_\mathrm{W})} \tag{9}$$

Where:

$U(\mathrm{ther})$ - calibration expanded uncertainty of the liquid thermometer, in $^\circ\mathrm{C}$ or K.

In general, if the calibration certificate of the thermometer is based upon a normal distribution of measurements with a high number of degrees of freedom the coverage factor will be $k=2$.

$u(\mathrm{res})$ – resolution of the used thermometer.

$u(\delta t)$ - estimation of the uncertainty caused by possible drift and ageing of the temperature measuring system after its calibration.

$u(\delta t_{\mathrm{W}})$ - evaluated uncertainty of the average water temperature caused by temperature differences (and temperature gradients) that can be measured or estimated between bottom and top of the instrument under calibration.

Note: the maximum temperature difference between various parts of water inside the vessel should be kept at to negligible values (10 mK to 20 mK). If necessary, the water can be carefully stirred with a rod soon after weighing (care has to be taken to ensure the rod is at the same temperature as the water before use to avoid heat transfer). If this is not possible, temperature can be measured in different, representative locations; having defined t_{max} and t_{min} as the highest and lowest temperatures found, the standard deviation of a rectangular distribution, namely $u(\delta t_{\mathrm{W}}) = (t_{\mathrm{max}} - t_{\mathrm{min}}) / \sqrt{12}$, is an upper limit for the uncertainty of the mean temperature.

$u(\delta t_{\mathrm{s}})$ - evaluated uncertainty caused by variation between the water temperature and temperature of the volume instrument (artefact) under calibration.

During the calibration the difference of temperature between air and water should be within definite limits, no more than 2 °C is recommended.

This uncertainty contribution $u(\delta t_{\mathrm{s}})$ should be evaluated considering that the temperature of the artefact is most near to the temperature of the water rather the temperature of the air.

A conservative approach, as in [12], can be used: $u(\delta t_{\mathrm{s}}) = \frac{|t_{\mathrm{A0}} - t_{\mathrm{W}}|}{8\sqrt{3}}$, where t_{A0} and t_{W} are temperature of measured air temperature and temperature of the water respectively.

6.3.3 Water density

The uncertainty of the water density should be evaluated according to the used formula and type of water (impurities, air content, etc).

The formulation provided by Tanaka [6] has an estimated standard uncertainty of $u(\rho_{\mathrm{W,form}}) = 4.5 \times 10^{-7}\,\mathrm{g/mL}$. However, this is the uncertainty of the formulation alone, therefore, the uncertainty of the purity $u(\delta\rho_{\mathrm{W}})$ and the contribution due to the temperature uncertainty of the water $u(\rho_{\mathrm{W,t}})$ (which depends on the expansion coefficient of the water β) must be added.

$$u(\rho_{\mathrm{W}}(t_{\mathrm{W}})) = \sqrt{u^2(\rho_{\mathrm{W,form}}) + u^2(\rho_{\mathrm{W,t}}) + u^2(\delta\rho_{\mathrm{W}})} \qquad (10)$$

where

$$u(\rho_{\mathrm{W,t}}) = u(t_{\mathrm{W}}) \times \beta \times \rho_{\mathrm{W}}(t_{\mathrm{W}})$$

The expansion coefficient can be estimated as it is described in [10].

$$\beta = \left(-0.1176 t_W^2 + 15.846 t_W - 62.677\right) \times 10^{-6} \ ^\circ\mathrm{C}^{-1} \quad (11)$$

If the information about the water preparation is insufficient or if it can be assumed that there is a possible water contamination, possibly occurring both at the beginning (residual contamination of the volumetric instrument) and at the end of calibration (newly introduced impurities), a correction with an associated uncertainty can be made.

The density of the working water can be measured or compared to that of a freshly prepared sample of pure water, typically by means of a high resolution (1 ppm) density meter. If no such measurement is carried out, an appropriate uncertainty contribution should be evaluated.

The standard uncertainty associate to $u\left(\delta\rho_W\right)$ might range from:

- a few ppm for highly pure water of known and controlled isotopic composition, or measured by means of a high-resolution density meter, typically used for glassware calibration.
- to 10 ppm for distilled or de-ionised water, provided that the conductivity is less than 5 µS/cm, typically used in proving tanks.
- to 20 ppm for lower quality distilled or de-ionised water from a reputable source, typically used in proving tanks.

6.3.4 Air density

The uncertainty of the air density should be evaluated according to the chosen formula [7,8,9] and the input uncertainties. For the purpose of this guide only the CIPM simplified air density formula is used. The relative standard uncertainty due to the formula is $u_{\mathrm{form}}/\rho_A = 2.4 \times 10^{-4}$.

In addition to the uncertainty u_{form}, the uncertainties of the estimates for p_A, h_r and t_A determine the total uncertainty $u\left(\rho_A\right)$, according to Appendix 1 of EURAMET cg 18.

$$u\left(\rho_A\right) = \rho_A \sqrt{\left(\frac{u_{pA}\left(\rho_A\right)}{\rho_A} \times u\left(p_A\right)\right)^2 + \left(\frac{u_{tA}\left(\rho_A\right)}{\rho_A} \times u\left(t_A\right)\right)^2 + \left(\frac{u_{hr}\left(\rho_A\right)}{\rho_A} \times u\left(h_r\right)\right)^2 + \left(\frac{u_{\mathrm{form}}\left(\rho_A\right)}{\rho_A}\right)^2} \quad (12)$$

Note 1: the air that is displaced by water is that inside the volumetric instrument. In case of “dry” volume determinations its density is equal to that of ambient air, therefore it is correct to measure pressure, temperature and relative humidity nearby. Also in case of internally wet volumetric instruments, the present practice is to measure the three parameters in ambient air. At 20 °C the maximum difference in density between dry and fully saturated air is + 0.9 %. However, the effect of humidity above 90 %rh inside the volumetric instrument is partially compensated by a generally lower temperature, caused by evaporation. The effects on air density of such internal temperature and humidity may deserve more attention, now that volume standards with reproducibility in the order of

0.001 % are available. In any case, it appears pointless to use accurate hygrometers and thermometers if humidity and temperature are not measured nearby. The proximity of nearby needs to be determined based on the type of volume instrument being calibrated. This should take into account the desired measurement uncertainty and the uncertainties associated with measuring humidity and temperature at that location, in comparison to the displaced air or water (depending on the filling or withdrawing method).

Note 2: Uncertainty of temperature of the air, air pressure and relative humidity have to include all relevant components, not only ones found on calibration certificates.

6.3.5 Density of reference weights

The value presented in the calibration certificate of the set of reference weights, or of the analytical balance can be used. Alternatively, the uncertainties corresponding to the used weight class according to OIML R 111-1 [11] can be used.

6.3.6 Cubic thermal expansion coefficient of the material of the calibrated instrument

The thermal expansion coefficient is dependent on knowledge of the actual material of the artifact and on the source of data which provides the user with an appropriate value. Data from the literature or manufacturer should be used and this would be expected to have an (standard) uncertainty of the order of 5 %.

$$u(\gamma) = 0.05\frac{\gamma}{\sqrt{3}}$$

6.3.7 Operator effect or reproducibility condition of measurement

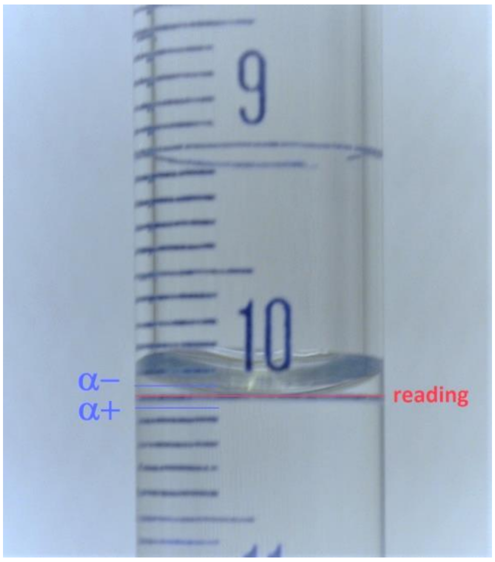
6.3.7.1 Meniscus reading

The variability of meniscus settings and scale readings made by a single operator depends upon individual expertise. This reading influences directly the experimental standard deviation; therefore, only Type B components of meniscus and scale reading uncertainty should be estimated and composed. These components are intended to take into account the unavoidable bias (or average deviations of the positioning of meniscus that is characteristic of a given operator in a given artefact) with reference to the ideal position defined by [4] (“the meniscus shall be set so that the plane of the upper edge of the graduation line is horizontally tangential to the lowest point of the meniscus, the line of sight being in the same plane”). It is recommended that the estimate of this contribution to uncertainty be separately declared in calibration certificates, in order to allow users (who are responsible for the evaluation of actual uncertainties occurring during the use of their own instrument) to estimate and compose a supplementary contribution in case they consider themselves unable to approximate the proper meniscus positioning within the same uncertainty limits.

Several approaches can be used to determine the uncertainty of the meniscus.

a) Uncertainty in reading the position of a concave meniscus with respect to a graduated scale

In this case the uncertainty due to the meniscus could be estimated as the uncertainty in the volume determination due to the resolution α of the scale of the volumetric apparatus. The usual practice is to assume a rectangular distribution (within $\alpha-$ and $\alpha+$) and estimate the standard uncertainty as $\alpha/2\sqrt{3}$. However, this approach could overestimate the actual reading uncertainty of the operator. Usually, the meniscus position is determined using optical aids and for this reason it is highly probable to take the reading closer to the right position of the meniscus tangentially to the corresponding scale mark than away from it. Therefore, it is recommended and more realistic to consider as an upper uncertainty limit the one which is estimated assuming for example a triangular distribution instead, as shown in Fig. 1.



Resolution:
$\alpha = 0.1$ mL
$\alpha+ = 10.05$ mL
$\alpha- = 9.95$ mL

Depending on the assumed distribution of the meniscus reading between positions α+ and α- , the uncertainty will be:

$u(\delta_{\text{men}}) = \frac{\alpha}{2\sqrt{3}} = 0.029$ mL
(rectangular)

$u(\delta_{\text{men}}) = \frac{\alpha}{2\sqrt{6}} = 0.020$ mL
(triangular)

Fig 1. Concave meniscus in a graduated volumetric device

b) Uncertainty in reading the position of a concave meniscus with respect to a one-mark

In this case the uncertainty in the volume due to the reading of the position of the meniscus could be evaluated as the product of two geometric factors:

- The uncertainty in the positioning and determination of the meniscus' lowest point, u_{p}.
- The area E of the cross section of the volumetric instrument where the air-water meniscus is located, which can be a cylindrical neck or a section of a different shape.

Therefore, the uncertainty due to meniscus reading is approximated as:

$$u(\delta V_E) = u_{\text{p}} \times E \tag{13}$$

As the quality of the engraving is one of the most important factors, a possible criterion for determining the uncertainty in setting and reading correctly the position of the lowest point of the meniscus surface is to assume that uncertainty not larger than one half of the width of the scale mark ($u_{\text{p}} = 0.5d$). However, a skilled operator can reduce his own uncertainty to a fraction of the width of the mark; the use of a simple magnifying glass in a good artefact may allow a standard uncertainty as low as 0.05 mm to be achieved.

Often determination of the diameter or an area of the cross section E of the neck of a volumetric instrument is not easy. In the case of graduated scales, the neck section can be determined by considering the total volume of the neck scale V_S and the extension in length of the scale L, where the cross section area E will be:

$$E = V_S / L \tag{14}$$

c) Uncertainty due to the formation of a convex meniscus

This type of meniscus is present in the case of overflow pipettes. The uncertainty due to meniscus formation is entirely attributed to the repeatability in the length of the short radius of the meniscus, since the area of its base is constant and equal to the cross section of the overflow pipe of the pipette.

6.3.7.2 Handling of volume instruments

There is a variability in the handling of volume instruments that should be included in the uncertainty calculation, this effect is critical in piston pipettes and can be quantified as a minimum of 0.1 % of the measured volume. The chosen value is based on long term experimental investigations of POVA manufacturers, calibration laboratories and proved by pilot studies. More information can be find in Guideline [15].

For other piston operated instruments other technical considerations can be found in [16] and [17].

6.3.8 Evaporation

Weighing of the filled instrument should be carried out as soon as possible after having set the meniscus in order to reduce errors due to any evaporation. When a procedure is adopted which requires the water contained in the instrument under calibration to be transferred into an auxiliary vessel installed on the balance, a correction caused by increased evaporation (or even minute loss through spray or droplet formation) from the water jet and bubbles produced in the receiving tank should be evaluated, together with its own contribution to uncertainty. The values described in EURAMET Calibration Guideline No. 21 [10], table 2 can also be used.

6.3.9 Measurement repeatability

Equation (15) is a possible expression for this Type A uncertainty component:

$$u\left(\delta V_{\text{rep}}\right) = \frac{s\left(V_0\right)}{\sqrt{n}} \tag{15}$$

Where:

$s\left(V_0\right)$ - standard deviation of a series of independent volume measurements, in mL

n - number of measurements

Note 1: The value of volume that will be given as a result of n repeated measurements is the arithmetic mean of the n results, therefore the type A uncertainty component is the standard deviation of the mean, $u\left(\delta V_{\mathrm{rep}}\right)$ as defined above. However, it is recommended that the number of measurements n and their standard deviation $s\left(V_0\right)$ be quoted in calibration reports or certificates, because if the user is going to make single, not averaged measurements, its type A uncertainty contribution will not be $u\left(\delta V_{\mathrm{rep}}\right)$, but the standard deviation of the whole population of possible measurements, which is evaluated by $s\left(V_0\right)$. For details on using such information from calibration certificates, please see chapter 6.3.3.1 in [10].

6.3.10 Other sources of uncertainty of the measurement

The listed components of uncertainty may not be exhaustive. If necessary, other contributions of uncertainty should be investigated by the laboratory.

6.4 Sensitivity coefficient of each input quantity

Defining the terms A, B and C by:

$\mathrm{A}=\dfrac{1}{\rho_{\mathrm{W}}-\rho_{\mathrm{A}}}$; $\mathrm{B}=1-\dfrac{\rho_{\mathrm{A}}}{\rho_{\mathrm{B}}}$; $\mathrm{C}=1-\gamma\left(t-t_0\right)$ and with $m=\left(I_{\mathrm{L}}-I_{\mathrm{E}}\right)$, equation (5) can be rewritten as:

$$V_0=m\times\mathrm{A}\times\mathrm{B}\times\mathrm{C}+\delta V_{\mathrm{op}}+\delta V_{\mathrm{evap}}+\delta V_{\mathrm{rep}} \tag{16}$$

This procedure saves some computational effort in developing the sensitivity coefficients, necessary for the computation of the combined standard uncertainty of V_0.

For each input quantity, it now present the results of the calculation of the sensitivity coefficient based on the new formulation of equation (5) as equation (16).

6.4.1 Mass

$$\left(\frac{\partial V_0}{\partial m}\right) = \mathrm{A}\times\mathrm{B}\times\mathrm{C} \tag{17}$$

6.4.2 Temperature

$$\left(\frac{\partial V_0}{\partial t}\right) = m\times\mathrm{A}\times\mathrm{B}\times(-\gamma) \tag{18}$$

6.4.3 Water density

$$\left(\frac{\partial V_0}{\partial \rho_\mathrm{W}}\right) = -m\times\mathrm{B}\times\mathrm{C}\times\frac{1}{\left(\rho_\mathrm{W}-\rho_\mathrm{A}\right)^2} = -m\times\mathrm{A}^2\times\mathrm{B}\times\mathrm{C} \tag{19}$$

6.4.4 Air density

$$\left(\frac{\partial V_0}{\partial \rho_\mathrm{A}}\right) = m\times\mathrm{C}\times\mathrm{A}\times\left[\frac{1}{\rho_\mathrm{W}-\rho_\mathrm{A}}\times\left(1-\frac{\rho_\mathrm{A}}{\rho_\mathrm{B}}\right)-\frac{1}{\rho_\mathrm{B}}\right] = m\times\mathrm{A}\times\mathrm{C}\times\left(\mathrm{B}\times\mathrm{A}-\frac{1}{\rho_\mathrm{B}}\right) \tag{20}$$

6.4.5 Density of the reference weights

$$\left(\frac{\partial V_0}{\partial \rho_\mathrm{B}}\right) = m\times\mathrm{A}\times\mathrm{C}\times\frac{\rho_\mathrm{A}}{\rho_\mathrm{B}^2} \tag{21}$$

6.4.6 Cubic thermal expansion coefficient of the material of the calibrated instrument

$$\left(\frac{\partial V_0}{\partial \gamma}\right) = m\times\mathrm{A}\times\mathrm{B}\times\left(-\left(t-t_0\right)\right) \tag{22}$$

6.4.7 Operator effect

$$\left(\frac{\partial V_0}{\partial V_\mathrm{op}}\right) = 1 \tag{23}$$

6.4.8 Evaporation

$$\left(\frac{\partial V_0}{\partial V_\mathrm{evap}}\right) = 1 \tag{24}$$

6.4.9 Measurement repeatability

$$\left(\frac{\partial V_0}{\partial V_\mathrm{rep}}\right) = 1 \tag{25}$$

6.5 Combined standard uncertainty of measurand

Within the hypothesis of the applicability of the propagation law of uncertainties, the combined standard uncertainty of the measurand is expressed as:

$$u^2(V_0) = \sum_i \left(\frac{\partial V_0}{\partial x_i} \times u(x_i) \right)^2 \tag{26}$$

Using the expressions of the parts 6.3. and 6.4., the resultant combined standard uncertainty of the measurand is:

$$u(V_0) = \left[\begin{array}{l} \left(\frac{\partial V_0}{\partial m}\right)^2 u^2(m) + \left(\frac{\partial V_0}{\partial t}\right)^2 u^2(t) + \left(\frac{\partial V_0}{\partial \rho_W}\right)^2 u^2(\rho_W) + \left(\frac{\partial V_0}{\partial \rho_A}\right)^2 u^2(\rho_A) + \\ + \left(\frac{\partial V_0}{\partial \rho_B}\right)^2 u^2(\rho_B) + \left(\frac{\partial V_0}{\partial \gamma}\right)^2 u^2(\gamma) + u^2(\delta V_{op}) + u^2(\delta V_{evap}) + u^2(\delta V_{rep}) \end{array} \right]^{\frac{1}{2}} \tag{27}$$

6.6 Evaluation of any existing covariances

Equation (26) and Equation (27) do not include any covariances terms. If some other correlations are identified they must be evaluated and introduced if influential.

6.7 Choice of an appropriate coverage factor (*k*)

Having computed the standard uncertainty of the measurand through the composition of all contributions, assuming that the distribution of the standard uncertainty is normal, effective degrees of freedom ν_{eff} , can be estimated by means of the Welch-Satterthwaite formula:

$$\nu_{eff} = \frac{u_V^4}{\sum_{i=1}^{N} \frac{u_i^4}{\nu_i}} \tag{28}$$

Where are:

u_V combined uncertainty of the determined volume

u_i standard uncertainty of each component

ν_i degrees of freedom

which allows to calculate an appropriate coverage factor (k) for a 95 % confidence level (see GUM Annex G).

6.8 Expanded uncertainty

With the value of the coverage factor k and of the combined standard uncertainty of the measurand, the expanded uncertainty is deduced by:

$$U = k \times u(V_0) \tag{29}$$

7 NUMERICAL EXAMPLES

7.1 Example 1 - Flask

In order to apply numerical values to the uncertainty calculation procedure described above, a 1000 mL volumetric flask was calibrated. The data is summarised in Table 1.

Table 1. Summary of data for gravimetric calibration of a 1000 mL volumetric flask (average values)

Input Quantity X_i	**Value of the input quantity** x_i	**Uncertainty equation number / sub-clause**
Mass (m)	996.9505 g	(7) / 6.3.1
Temperature (water) (t)	19.11 °C	(8) / 6.3.2
Water density ($\rho_W(t_W)$)	0.9984 g/mL	(10) / 6.3.3
Air density (ρ_A)	0.0012 g/mL	(12) / 6.3.4
Density of the reference weights (ρ_B)	8.00 g/mL	- / 6.3.5
Cubic thermal expansion coefficient of the flask material (γ)	1×10^{-5} °C^{-1}	- / 6.3.6
Uncertainty contribution	**Value**	**Distribution / sub-clause**
Meniscus reading of the flask (δV_{men})	0.015 mL	Rectangular / 6.3.7.1
Evaporation (δV_{evap})	0	- / 6.3.8 b)
Measurement repeatability ($s(V_0)$)	0.044 mL	Normal / 6.3.9

After analysing the measurement problem (7.1) and determining the volume of the volumetric flask according to the correct mathematical model, equation (1), $V_{20} = 999.628 \text{ mL}$, it is necessary to determine the standard uncertainty of each input quantity, the sensitivity coefficients, the combined uncertainty, the effective degrees of freedom, the corresponding coverage factor and finally the expanded uncertainty. The pertinent aspects of this example as discussed in this Guide and the followings sub clauses are summarized in Table 2.

7.1.1 Determination of the standard uncertainty of each input quantity

7.1.1.1 Mass

The standard uncertainty of the mass (for both I_L and I_E) was obtained from the value of the calibration of the weighing scale $U(\text{bal}) = 0,0018 \text{ g}$, using a coverage factor of 2 and from the resolution of the weighing scale $u(\text{res}) = 0.000029 \text{ g}$, using a rectangular distribution, then:

$$u(I_L) = u(I_E) = \sqrt{u^2(\text{bal}) + u^2(\text{res})} = \sqrt{\left(\frac{0.0018\ \text{g}}{2}\right)^2 + \left(\frac{\frac{0.0001\ \text{g}}{2}}{\sqrt{3}}\right)^2} = 0.0009\ \text{g}$$

If its considered that the correlations can be neglected and that $\delta m = 0$, equation (7) can be rewritten as:

$$u(m) = \sqrt{u^2(I_L) + u^2(I_E)} = \sqrt{(0.0009\ \text{g})^2 + (0.0009\ \text{g})^2} = 0.0013\ \text{g}$$

7.1.1.2 Temperature (water and volume instruments)

The standard uncertainty of the water temperature was obtained from the value of the thermometer calibration $U(\text{ther}) = 0.009\ °\text{C}$, using a coverage factor of 2 and from the resolution of the thermometer $u(\text{res}) = 0.00029\ °\text{C}$, using a rectangular distribution. If we consider $\delta t = 0$ and $\delta t_W = 0$, equation (9) can be rewritten as:

$$u(t_W) = \sqrt{\left(\frac{U(\text{ther})}{\text{k}}\right)^2 + u^2(\text{res})} = \sqrt{\left(\frac{0.009\ °\text{C}}{2}\right)^2 + \left(\frac{\frac{0.001\ °\text{C}}{2}}{\sqrt{3}}\right)^2} = 0.0045\ °\text{C}$$

Considering that the difference between air temperature and water temperature was $0.2\ °\text{C}$.

$$u(\delta t_s) = \frac{0.20\ °\text{C}}{8\sqrt{3}} = 0.014\ °\text{C}$$

Then,

$$u(t) = \sqrt{u^2(t_W) + u^2(\delta t_s)} = \sqrt{(0.0045\ °\text{C})^2 + (0.014\ °\text{C})^2} = 0.015\ °\text{C}$$

7.1.1.3 Water density

The standard uncertainty of the water density was obtained from the value provided by equation (in 6.3.3). The formulation provided by Tanaka [6] has an estimated standard uncertainty of $u(\rho_{\text{W,form}}) = 4.5 \times 10^{-7}\ \text{g/mL}$, the uncertainty due to the temperature of the water is $u(\rho_{\text{W,t}}) = 1.024 \times 10^{-6}\ \text{g/mL}$ and the uncertainty due to the purity of the water (5 ppm)

Is $u(\delta\rho_W) = 2.88 \times 10^{-6}\ \text{g/mL}$, then:

$$u\left(\rho_{W}\left(t_{W}\right)\right)=\sqrt{\left(4.5\times10^{-7}\ \text{g/mL}\right)^{2}+\left(1.24\times10^{-6}\ \text{g/mL}\right)^{2}+\left(2.88\times10^{-6}\ \text{g/mL}\right)^{2}}=$$
$$=3.09\times10^{-6}\ \text{g/mL}$$

7.1.1.4 Air density

The relative standard uncertainty of the air density CIPM simplified formula is $u_{\text{form}}\left(\rho_{A}\right)=2.4\times10^{-4}\ \text{g/mL}$. Considering the uncertainty values form the calibration of the pressure, temperature and humidity sensor, the uncertainty due to the temperature of the air is $0.16\ °\text{C}$, the uncertainty due to the barometric pressure is $6\ \text{Pa}$, the uncertainty due to the relative humidity is $0.6\ \%$, then considering the sensitivity coefficients described in Appendix A of [8]:

$$u\left(\rho_{A}\right)=0.0012\times\left[\begin{array}{l}\left(-4\times10^{-3}\times\frac{0.16}{2}\right)^{2}+\left(1\times10^{-5}\times\frac{60}{2}\right)^{2}+\\+\left(-9\times10^{-3}\times\frac{0.006}{2}\right)^{2}+\left(2.4\times10^{-4}\right)^{2}\end{array}\right]^{\frac{1}{2}}=$$
$$=1.76\times10^{-6}\ \text{g/mL}$$

7.1.1.5 Density of reference weights

The value presented in the calibration certificate of the set of masses was used $0.06\ \text{g/mL}$, at which a coverage factor of 2 is associated:

$$u\left(\rho_{B}\right)=\frac{0.06\ \text{g/mL}}{2}=0.03\ \text{g/mL}$$

7.1.1.6 Cubic thermal expansion coefficient of the material of the calibrated instrument

The thermal expansion coefficient of the flask is given by the manufacturer as $\gamma=1\times10^{-5}\ °\text{C}^{-1}$, in the lack of a more informative statement, a rectangular probability distribution of ± 5% is assumed. The relevant standard uncertainty is therefore:

$$u\left(\gamma\right)=\frac{5\times10^{-7}\ °\text{C}^{-1}}{\sqrt{3}}=2.89\times10^{-7}\ °\text{C}^{-1}$$

7.1.1.7 Meniscus reading

The meniscus position was determined using optical aids and for this reason the standard uncertainty with a rectangular probability distribution is:

$$u\left(\delta V_{\text{men}}\right)=\frac{0.015\ \text{mL}}{\sqrt{3}}=0.009\ \text{mL}$$

7.1.1.8 Evaporation

Weighing of the flask was carried out as soon as possible after having set the meniscus, therefore the errors and uncertainty due to any evaporation are negligible. The evaporation contribution can also be neglected if a stopper is used with the volume instruments, whenever possible.

7.1.1.9 Measurement repeatability

Following equation (15), the type A uncertainty component can be determined by:

$$u\left(\delta V_{\mathrm{rep}}\right)=\frac{s\left(V_0\right)}{\sqrt{n}}=\frac{0.044\ \mathrm{mL}}{\sqrt{10}}=0.014\ \mathrm{mL}$$

7.1.2 Sensitivity coefficient of each input quantity

For each input quantity, the results of the calculation of the sensitivity coefficient are presented below, taken into account equation (16).

7.1.2.1 Mass

$$\left(\frac{\partial V_0}{\partial m}\right)=\mathrm{A}\times\mathrm{B}\times\mathrm{C}=1\ \mathrm{mL/g}$$

7.1.2.2 Temperature (water and volume instrument)

$$\left(\frac{\partial V_0}{\partial t}\right)=m\times\mathrm{A}\times\mathrm{B}\times\left(-\gamma\right)=-1\times10^{-2}\ \mathrm{mL/°C}$$

7.1.2.3 Water density

$$\left(\frac{\partial V_0}{\partial \rho_{\mathrm{W}}}\right)=-m\times\mathrm{B}\times\mathrm{C}\times\frac{1}{\left(\rho_{\mathrm{W}}-\rho_{\mathrm{A}}\right)^2}=-m\times\mathrm{A}^2\times\mathrm{B}\times\mathrm{C}=\text{-}1003\ \left(\mathrm{mL}\right)^2/\mathrm{g}$$

7.1.2.4 Air density

$$\left(\frac{\partial V_0}{\partial \rho_{\mathrm{A}}}\right)=m\times\mathrm{C}\times\mathrm{A}\times\left[\frac{1}{\rho_{\mathrm{W}}-\rho_{\mathrm{A}}}\times\left(1-\frac{\rho_{\mathrm{A}}}{\rho_{\mathrm{B}}}\right)-\frac{1}{\rho_{\mathrm{B}}}\right]=m\times\mathrm{A}\times\mathrm{C}\times\left(\mathrm{B}\times\mathrm{A}-\frac{1}{\rho_{\mathrm{B}}}\right)=877\ \left(\mathrm{mL}\right)^2/\mathrm{g}$$

7.1.2.5 Density of reference weights

$$\left(\frac{\partial V_0}{\partial \rho_{\mathrm{B}}}\right)=m\times\mathrm{A}\times\mathrm{C}\times\frac{\rho_{\mathrm{A}}}{\rho_{\mathrm{B}}^2}=1.88\times10^{-2}\ \left(\mathrm{mL}\right)^2/\mathrm{g}$$

7.1.2.6 Cubic thermal expansion coefficient of the material of the flask

$$\left(\frac{\partial V_0}{\partial \gamma}\right)=m\times\mathrm{A}\times\mathrm{B}\times\left(-\left(t-t_0\right)\right)=890.66\ \mathrm{°C\ mL}$$

7.1.2.7 Meniscus reading

$$\left(\frac{\partial V_0}{\partial \delta V_{\mathrm{men}}}\right)=1$$

7.1.3 Combined standard uncertainty of measurand

The combined uncertainty $u\left(V_{20}\right)$ is calculated from the equation (27). The individual terms are collected and substituted into this expression to obtain:

$$u\left(V_{20}\right)=\begin{bmatrix}\left(\frac{\partial V_0}{\partial m}\right)^2 u^2\left(m\right)+\left(\frac{\partial V_0}{\partial t}\right)^2 u^2\left(t\right)+\left(\frac{\partial V_0}{\partial \rho_W}\right)^2 u^2\left(\rho_W\right)+\left(\frac{\partial V_0}{\partial \rho_A}\right)^2 u^2\left(\rho_A\right)+ \\ \left(\frac{\partial V_0}{\partial \rho_B}\right)^2 u^2\left(\rho_B\right)+\left(\frac{\partial V_0}{\partial \gamma}\right)^2 u^2\left(\gamma\right)+u^2\left(\delta V_{op}\right)+u^2\left(\delta V_{evap}\right)+u^2\left(\delta V_{rep}\right)\end{bmatrix}^{\frac{1}{2}}=0.017 \text{ mL}$$

7.1.4 Evaluation of any existing covariances

The significant covariances were evaluated in section 6.3.1.

7.1.5 Choice of an appropriate coverage factor (*k*)

To calculate the coverage factor (k), it's necessary to estimate the effective degrees of freedom ν_{eff}, using the Welch-Satterthwaite formula:

$$\nu_{eff}\left(V_{20}\right)=\frac{u_V^4}{\sum_{i=1}^{N}\frac{u_i^4}{\nu_i}}=\frac{u_{V20}^4}{\frac{u^4(m)}{\nu(m)}+\frac{u^4(t)}{\nu(t)}+\frac{u^4(\rho_W)}{\nu(\rho_W)}+\frac{u^4(\rho_A)}{\nu(\rho_A)}+\frac{u^4(\rho_B)}{\nu(\rho_B)}+\frac{u^4(\gamma)}{\nu(\gamma)}+\frac{u^4(\delta V_{men})}{\nu(\delta V_{men})}+\frac{u^4(\delta V_{rep})}{\nu(\delta V_{rep})}}$$

$\nu_{eff}\left(V_{20}\right)=19$, which gives a coverage factor k = 2.15 for a corresponding coverage probability of approximately 95 %.

7.1.6 Expanded uncertainty

The expanded uncertainty is deduced by:

$$U = k \times u(V_0) = 2.15 \times 0.017 = 0.036 \text{ mL}$$

The numerical example described above is summarised in the following table.

Table 2. Summary for the standard uncertainty components

Quantity x_i	Estimate x_i	Standard uncertainty component $u(x_i)$	Value of standard uncertainty $u(x_i)$	$c_i \equiv \frac{\partial f}{\partial x_i}$	$u_i = c_i \times u(x_i)$ (mL)	Degrees of freedom
Mass	996.9505 g	$u(m)$	0.00127 g	1.00 mL/g	1.27×10^{-3}	50
Temperature (water and volume instrument)	19.11 ºC	$u(t)$	0.0152 ºC	-1×10^{-2} mL/ºC	$- 1.52 \times 10^{-4}$	∞
Water density	0.9984 g/mL	$u(\rho_W)$	3.09×10^{-6} g/mL	-1000 mL^2/g	$- 3.10 \times 10^{-3}$	∞
Air density	0.0012 g/mL	$u(\rho_A)$	1.76×10^{-6} g/mL	877 mL^2/g	1.55×10^{-3}	∞
Density of the reference weigths	8.00 g/mL	$u(\rho_B)$	0.0346 g/mL	1.88×10^{-2} mL^2/g	6.53×10^{-4}	∞
Coefficient of thermal expansion from the flask material	1×10^{-5} °C^{-1}	$u(\gamma)$	2.89×10^{-7} °C^{-1}	-890.66 ºC mL	$- 2.57 \times 10^{-4}$	∞
Meniscus reading	0	$u(\delta V_{men})$	0.00866 mL	1	0.00866	∞
Measurement Repeatability	0	$u(\delta V_{rep})$	0.014 mL	1	0.014	9
					$u(V_{20}) = 0.017$ mL $\nu_{eff}(V_{20}) = 19$ $k = 2.15$ $U(V_{20}) = 0.036$ mL	

7.2 Example 2 - Pycnometer

In order to apply numerical values to the uncertainty calculation procedure described above, a 100 mL glass pycnometer was calibrated. The data is summarised in Table 3.

Table 3. Summary of data for gravimetric calibration of a 100 mL glass pycnometer (average values)

Input Quantity X_i	**Value of the input quantity** x_i	**Uncertainty equation number / sub-clause**
Mass (m)	99.7500 g	(7) / 6.3.1
Temperature (water) (t)	18.94 °C	(8) / 6.3.2
Water density ($\rho_W(t_W)$)	0.9984 g/mL	(10) / 6.3.3
Air density (ρ_A)	0.0012 g/mL	(12) / 6.3.4
Density of the reference weights (ρ_B)	8.00 g/mL	- / 6.3.5
Cubic thermal expansion coefficient of the flask material (γ)	1×10^{-5} °C^{-1}	- / 6.3.6
Uncertainty contribution	**Value**	**Distribution / sub-clause**
Meniscus reading of the flask (δV_{men})	0	Rectangular / 6.3.7.1
Evaporation	0	- / 6.3.8 b)
Measurement repeatability ($s(V_0)$)	0.0026 mL	Normal / 6.3.9

After analysing the measurement problem (7.2) and determining the volume of the glass pycnometer according to the correct mathematical model, equation (1), $V_{20} = 100.014\ \text{mL}$, it is necessary to determine the standard uncertainty of each input quantity, the sensitivity coefficients, the combined uncertainty, the effective degrees of freedom, the corresponding coverage factor and finally the expanded uncertainty. The pertinent aspects of this example as discussed in this Guide and the followings sub clauses are summarized in Table 3.

7.2.1 Determination of the standard uncertainty of each input quantity

7.2.1.1 Mass

The standard uncertainty of the mass (for both I_L and I_E) was obtained from the value of the calibration of the weighing scale $U(\text{bal}) = 0{,}00015\ \text{g}$, using a coverage factor of 2 and from the resolution of the weighing scale $u(\text{res}) = 0.000029\ \text{g}$, using a rectangular distribution, then:

$$u(I_L)=u(I_E)=\sqrt{u^2(\text{bal})+u^2(\text{res})}=\sqrt{\left(\frac{0.00015\ \text{g}}{2}\right)^2+\left(\frac{\frac{0.0001\ \text{g}}{2}}{\sqrt{3}}\right)^2}=0.000080\ \text{g}$$

If it is considered that the correlations can be neglected and that $\delta m=0$, equation (7) can be rewritten as:

$$u(m)=\sqrt{u^2(I_L)+u^2(I_E)}=\sqrt{(0.00008\ \text{g})^2+(0.00008\ \text{g})^2}=0.00011\ \text{g}$$

7.2.1.2 Temperature (water and volume instruments)

The standard uncertainty of the water temperature was obtained from the value of the thermometer calibration $U(\text{ther})=0.009\ °\text{C}$, using a coverage factor of 2 and from the resolution of the thermometer $u(\text{res})=0.00029\ °\text{C}$, using a rectangular distribution. If it is consider $\delta t=0$ and $\delta t_W=0$, equation (9) can be rewritten as:

$$u(t_W)=\sqrt{\left(\frac{U(\text{ther})}{\text{k}}\right)^2+u^2(\text{res})}=\sqrt{\left(\frac{0.009\ °\text{C}}{2}\right)^2+\left(\frac{\frac{0.001\ °\text{C}}{2}}{\sqrt{3}}\right)^2}=0.0045\ °\text{C}$$

Considering that the difference between air temperature and water temperature was $0.23\ °\text{C}$.

$$u(\delta t_s)=\frac{0.23\ °\text{C}}{8\sqrt{3}}=0.016\ °\text{C}$$

Then,

$$u(t)=\sqrt{u^2(t_W)+u^2(\delta t_s)}=\sqrt{(0.0045\ °\text{C})^2+(0.016\ °\text{C})^2}=0.017\ °\text{C}$$

7.2.1.3 Water density

The standard uncertainty of the water density was obtained from the value provided by equation (in 6.3.3). The formulation provided by Tanaka [6] has an estimated standard uncertainty of $u(\rho_{W,\text{form}})=4.5\times10^{-7}\text{g/mL}$, the uncertainty due to the temperature of the water is $u(\rho_{W,t})=1.01\times10^{-6}\ \text{g/mL}$ and the uncertainty due to the purity of the water is $u(\delta\rho_W)=2.88\times10^{-6}\ \text{g/mL}$, then:

$$u(\rho_W(t_W))=\sqrt{(4.5\times10^{-7}\ \text{g/mL})^2+(1.01\times10^{-6}\ \text{g/mL})^2+(2.88\times10^{-6}\ \text{g/mL})^2}=$$
$$=3.09\times10^{-6}\ \text{g/mL}$$

7.2.1.4 Air density

The relative standard uncertainty of the air density CIPM simplified formula is $u_{\text{form}}(\rho_A)=2.4\times10^{-4}\ \text{g/mL}$. Considering the uncertainty values from the calibration of the pressure, temperature and humidity sensor, the uncertainty due to the temperature of the air is $0.16\ °\text{C}$, the uncertainty due to the barometric pressure is $6\ \text{Pa}$, the uncertainty due to the relative humidity is $0,6\ \%$, then considering the sensitivity coefficients described in Appendix A of [8]:

$$u(\rho_A) = 0.0012 \times \left[\left(-4\times10^{-3}\times\frac{0.16}{2}\right)^2 + \left(1\times10^{-5}\times\frac{6}{2}\right)^2 + \right. \\ \left. + \left(-9\times10^{-3}\times\frac{0.006}{2}\right)^2 + \left(2.4\times10^{-4}\right)^2 \right]^{\frac{1}{2}} =$$

$$= 1.74\times10^{-6}\ \text{g/mL}$$

7.2.1.5 Density of reference weights

The value presented in the calibration certificate of the set of masses was used, $0.06\ \text{g/mL}$, at which a coverage factor of 2 is associated:

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

7.2.1.6 Cubic thermal expansion coefficient of the material of the calibrated instrument

The thermal expansion coefficient of the flask is given by the manufacturer as $\gamma = 1\times10^{-5}\ °\text{C}^{-1}$, in the lack of a more informative statement, a rectangular probability distribution of ± 5 % is assumed. The relevant standard uncertainty is therefore:

$$u(\gamma) = \frac{5\times10^{-7}\ °\text{C}^{-1}}{\sqrt{3}} = 2.89\times10^{-7}\ °\text{C}^{-1}$$

7.2.1.7 Meniscus reading

The meniscus contribution is considered negligible.

7.2.1.8 Evaporation

The evaporation contribution can be considered negligible in a pycnometer calibration.

7.2.1.9 Measurement repeatability

Following equation (15), the type A uncertainty component can be determined by:

$$u\left(\delta V_{\text{rep}}\right) = \frac{s(V_0)}{\sqrt{n}} = \frac{0.0026\ \text{mL}}{\sqrt{10}} = 0.0008\ \text{mL}$$

7.2.2 Sensitivity coefficient of each input quantity

For each input quantity, the results of the calculation of the sensitivity coefficient are presented below, taken into account equation (16).

7.2.2.1 Mass

$$\left(\frac{\partial V_0}{\partial m}\right) = \text{A}\times\text{B}\times\text{C} = 1\ \text{mL/g}$$

7.2.2.2 Temperature (water and volume instrument)

$$\left(\frac{\partial V_0}{\partial t}\right) = m\times\text{A}\times\text{B}\times(-\gamma) = -1\times10^{-3}\ \text{mL/°C}$$

7.2.2.3 Water density

$$\left(\frac{\partial V_0}{\partial \rho_\mathrm{W}}\right) = -m \times \mathrm{B} \times \mathrm{C} \times \frac{1}{\left(\rho_\mathrm{W} - \rho_\mathrm{A}\right)^2} = -m \times \mathrm{A}^2 \times \mathrm{B} \times \mathrm{C} = \text{-}100\ \left(\mathrm{mL}\right)^2/\mathrm{g}$$

7.2.2.4 Air density

$$\left(\frac{\partial V_0}{\partial \rho_\mathrm{A}}\right) = m \times \mathrm{C} \times \mathrm{A} \times \left[\frac{1}{\rho_\mathrm{W} - \rho_\mathrm{A}} \times \left(1 - \frac{\rho_\mathrm{A}}{\rho_\mathrm{B}}\right) - \frac{1}{\rho_\mathrm{B}}\right] = m \times \mathrm{A} \times \mathrm{C} \times \left(\mathrm{B} \times \mathrm{A} - \frac{1}{\rho_\mathrm{B}}\right) = 87.8\ \left(\mathrm{mL}\right)^2/\mathrm{g}$$

7.2.2.5 Density of reference weights

$$\left(\frac{\partial V_0}{\partial \rho_\mathrm{B}}\right) = m \times \mathrm{A} \times \mathrm{C} \times \frac{\rho_\mathrm{A}}{\rho_\mathrm{B}^2} = 1.86 \times 10^{-3}\ \left(\mathrm{mL}\right)^2/\mathrm{g}$$

7.2.2.6 Cubic thermal expansion coefficient of the material of the flask

$$\left(\frac{\partial V_0}{\partial \gamma}\right) = m \times \mathrm{A} \times \mathrm{B} \times \left(-\left(t - t_0\right)\right) = 106.37\ ^\circ\mathrm{C\ mL}$$

7.2.2.7 Meniscus reading

$$\left(\frac{\partial V_0}{\partial \delta V_\mathrm{men}}\right) = 1$$

7.2.3 Combined standard uncertainty of measurand

The combined uncertainty $u\left(V_{20}\right)$ is calculated from the equation (27). The individual terms are collected and substituted into this expression to obtain:

$$u\left(V_{20}\right) = \begin{bmatrix} \left(\frac{\partial V_0}{\partial m}\right)^2 u^2\left(m\right) + \left(\frac{\partial V_0}{\partial t}\right)^2 u^2\left(t\right) + \left(\frac{\partial V_0}{\partial \rho_\mathrm{W}}\right)^2 u^2\left(\rho_\mathrm{W}\right) + \left(\frac{\partial V_0}{\partial \rho_\mathrm{A}}\right)^2 u^2\left(\rho_\mathrm{A}\right) + \\ \left(\frac{\partial V_0}{\partial \rho_\mathrm{B}}\right)^2 u^2\left(\rho_\mathrm{B}\right) + \left(\frac{\partial V_0}{\partial \gamma}\right)^2 u^2\left(\gamma\right) + u^2\left(\delta V_\mathrm{op}\right) + u^2\left(\delta V_\mathrm{evap}\right) + u^2\left(\delta V_\mathrm{rep}\right) \end{bmatrix}^{\frac{1}{2}} = 8.9 \times 10^{-4}\ \mathrm{mL}$$

7.2.4 Evaluation of any existing covariances

The significant covariances were evaluated in section 6.3.1.

7.2.5 Choice of an appropriate coverage factor (*k*)

To calculate the coverage factor (*k*), it's necessary to estimate the effective degrees of freedom ν_eff, using the Welch-Satterthwaite formula:

$$\nu_\mathrm{eff}\left(V_{20}\right) = \frac{u_V^4}{\sum_{i=1}^{N} \frac{u_i^4}{\nu_i}} = \frac{u_{V20}^4}{\frac{u^4(m)}{\nu(m)} + \frac{u^4(t)}{\nu(t)} + \frac{u^4(\rho_\mathrm{W})}{\nu(\rho_\mathrm{W})} + \frac{u^4(\rho_\mathrm{A})}{\nu(\rho_\mathrm{A})} + \frac{u^4(\rho_\mathrm{B})}{\nu(\rho_\mathrm{B})} + \frac{u^4(\gamma)}{\nu(\gamma)} + \frac{u^4(\delta \mathrm{V}_\mathrm{men})}{\nu(\delta \mathrm{V}_\mathrm{men})} + \frac{u^4\left(\delta \mathrm{V}_\mathrm{rep}\right)}{\nu\left(\delta \mathrm{V}_\mathrm{rep}\right)}}$$

$\nu_\mathrm{eff}\left(V_{20}\right) = 13$, which gives a coverage factor $k = 2.21$ for a corresponding coverage probability of approximately 95 %.

7.2.6 Expanded uncertainty

The expanded uncertainty is deduced by:

$$U = k \times u(V_0) = 2.21 \times (8.9 \times 10^{-4}) = 2.0 \times 10^{-3} \text{ mL}$$

The numerical example described above is summarised in the following table.

Table 4. Summary for the standard uncertainty components for the glass pycnometer

Quantity x_i	Estimate x_i	Standard uncertainty component $u(x_i)$	Value of standard uncertainty $u(x_i)$	$c_i \equiv \frac{\partial f}{\partial x_i}$	$u_i = c_i \times u(x_i)$ (mL)	Degrees of freedom
Mass	99.7500 g	$u(m)$	0.000114 g	1.00 mL/g	1.14 × 10^{-4}	50
Temperature (water and volume instrument)	18.94 ºC	$u(t)$	0.017 ºC	-1×10^{-3} mL/ºC	- 1.70 × 10^{-5}	∞
Water density	0.9984 g/mL	$u(\rho_W)$	3.09 × 10^{-6} g/mL	-100 mL²/g	- 3.10 × 10^{-4}	∞
Air density	0.0012 g/mL	$u(\rho_A)$	1.74 × 10^{-6} g/mL	87.8 mL²/g	1.53 × 10^{-4}	∞
Density of the reference weigths	8.00 g/mL	$u(\rho_B)$	0.0346 g/mL	1.86 × 10^{-3} mL²/g	6.46 × 10^{-5}	∞
Coefficient of thermal expansion from the flask material	1×10^{-5} °C^{-1}	$u(\gamma)$	2.89 × 10^{-7} °C^{-1}	106.37 ºC mL	3.07 × 10^{-5}	∞
Measurement repeatability	0	$u(\delta V_{rep})$	0.0008 mL	1	0.0008	9
					$u(V_{20}) = 0.89$ µL $\nu_{eff}(V_{20}) = 1727$ $k = 2.21$ $U(V_{20}) = 2.0$ µL	

8 REFERENCES

1. JCGM 100:2008 (GUM), Evaluation of measurement data – Guide to the expression of uncertainty in measurement
2. JCGM 200:2012 (VIM), International Vocabulary of Metrology – Basic and General Concepts and Associated Terms, 3rd edition with minor corrections
3. ISO 3696:1987 – Water for analytical laboratory use - Specification and test methods
4. ISO 4787:2021 - Laboratory glass and plastic ware - Volumetric instruments - Methods for testing of capacity and for use
5. Batista, E., Paton R. The selection of water property formulae for volume and flow calibration, Metrologia, 2018, 55, 731-746
6. Tanaka, M., et. al; Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports, Metrologia, 2001, 38, 301-309
7. A. Picard, R.S. Davis, M. Glaser and K Fujii, Revised formula for the density of moist air Metrologia, 2008, Vol. 45, p 149-145
8. EURAMET Calibration Guideline No. 18 (2015) - Guidelines on the Calibration of Non-Automatic Weighing Instruments
9. F. Spieweck; H. Bettin, Review: Solid and liquid density determination, Tm-Technisches Messen 59 (1992) 7/8
10. EURAMET Calibration Guideline No. 21 (2024) - Guidelines on the Calibration of Standard Capacity Measures Using the Volumetric Method
11. OIML R 111:2004 - Weights of classes E1, E2, F1, F2, M1, M2, M3
12. ISO 7507-1:2003 Petroleum and liquid petroleum products – Calibration of vertical cylindrical tanks
13. ISO 8655:2022 - Piston-operated volumetric apparatus
14. OIML R120:2010 – Standard capacity measures for testing measuring systems for liquids other than water
15. Guideline DKD-R 8-1“Calibration of piston-operated pipettes with air cushions” Edition 12/2011, Revision 1; https://doi.org/10.7795/550.20240415.
16. Guideline DKD-R 8-2 “Calibration of Multiple Delivery Dispensers” Edition 01/2018, Revision 1; https://doi.org/10.7795/550.20240528
17. Guideline DKD-R 8-3 “Calibration of single stroke dispensers and piston burettes”; Edition 03/2020; https://doi.org/10.7795/550.20200401

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