

# 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 3.0 was developed thanks to the cooperation of Elsa Batista (IPQ, Portugal), Andrea Malengo, (INRIM, Italy), Zoe Metaxiotou (EIM, Greece), Alfonso Lobo Robledo, (CEM, Spain), Umit Akcadag (UME, Turkey) and Ljiljana Micic (DMDM, Serbia).

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EURAMET e.V.  
Bundesallee 100  
D-38116 Braunschweig  
Germany

E-Mail: [secretariat@euramet.org](mailto:secretariat@euramet.org)

Phone: +49 531 592 1960

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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 international recommendation [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.

- Laboratory glassware - Flasks
- Laboratory glassware – Pipettes
- Laboratory glassware – Cylinders
- Laboratory glassware - Burettes
- Pycnometers
- Standard test measures
- Proving tanks
- Overflow pipettes
- Piston operated instruments

## 2 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, 3<sup>rd</sup> edition with minor corrections
- [3] ISO 3696 (1987) – Water for analytical laboratory use: specification and test methods
- [4] ISO 4787 (2010) - Laboratory glassware - Volumetric glassware - Methods for use and testing of capacity

- [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 (2013) - 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

### 3 TERMINOLOGY AND SYMBOLS

The terminology used in this document is mainly based on existing documents, GUM [1] and VIM [2].

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

### 4 GRAVIMETRIC METHOD

The gravimetric method is the standard method used both by National Metrology Institutes (NMIs) 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):

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

Where:

- $V_0$  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
- $\rho_W$  liquid density, in g/mL, at the calibration temperature  $t$ , in °C, according to equation (2)
- $\rho_A$  air density, in g/mL, according to equation (4)

- $\rho_B$  density of the reference weights used during measurement (substitution) or during calibration of the balance, assumed to be 8.0 g/mL
- $\gamma$  cubic thermal expansion coefficient of the material of the instrument under calibration, in  $^{\circ}\text{C}^{-1}$ . (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  $^{\circ}\text{C}$
- $t_0$  reference temperature, in  $^{\circ}\text{C}$

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 weighings. 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.

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 standardization:

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

Where:

$t$  = water temperature, in  $^{\circ}\text{C}$

$a_1$  = -3.983035  $^{\circ}\text{C}$

$a_2$  = 301.797  $^{\circ}\text{C}$

$a_3$  = 522528.9 ( $^{\circ}\text{C}$ )<sup>2</sup>

$a_4$  = 69.34881  $^{\circ}\text{C}$

$a_5$  = 0.999974950 g/mL

Note:  $a_5$  is the maximum density value of SMOW water in one atmosphere (at 3.98  $^{\circ}\text{C}$ ). 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]:

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

Where:

$t$  = water temperature, in  $^{\circ}\text{C}$

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

$$s_1 = 0.106 \times 10^{-6} \text{ g/mL}^\circ\text{C}$$

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 air density can be determined according to the formula for the density of moist air - CIPM-2007, described in [7]:

$$\rho_A / (10^{-3} \text{ kg} \cdot \text{m}^{-3}) = \left[ 3.483740 + 1.4446 \times (x_{CO_2} - 0.0004) \right] \times \frac{p}{ZT} \times (1 - 0.3780 \times x_v) \quad (4)$$

$p$  barometric pressure, in Pa

$T$  thermodynamic temperature = 273.15 +  $t$  / °C, in K

$x_v$  mole fraction of water vapor

$x_{CO_2}$  mole fraction of carbon dioxide in laboratory air

$Z$  compressibility factor

The simplified CIPM formula for the air density can also be used under the constraints given below [8]:

$$\rho_A = \frac{0.34848p - 0.009h_r \exp(0.061t)}{t + 273.15} \text{ kg/m}^3 \quad (5)$$

$t$  ambient temperature, in °C

$p$  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  $2.4 \times 10^{-4}$ .

Another common used formula for air density is described in Spieweck's work [9].

## **5 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.

### **5.1 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.

### **5.2 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 have to be established.

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

### **5.3 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.

### **5.4 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, 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.

### **5.5 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).

## 6 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.

## 7 PROCEDURE FOR CALCULATING UNCERTAINTY IN GRAVIMETRIC DETERMINATION OF VOLUME

### 7.1 Mathematical expression of the volume $V_0$

$$V_0 = \frac{m}{\rho_W(t_W) - \rho_A(t_A, p_A, h_T)} \times \left( 1 - \frac{\rho_A(t_A, p_A, h_T)}{\rho_B} \right) \times [1 - \gamma(t - t_0)] + \delta V_{op} + \delta V_{evap} + \delta V_{rep} \quad (6)$$

with

$$m = (I_L - I_E) + \delta m$$

$$t_W = t_{W0} + \delta t_W$$

$$t_A = t_{A0} + \delta t_A$$

$$t = t_W + \delta t_S$$

$$\rho_W(t_W) = \rho_{W,form}(t_W) + \delta \rho_{W,form}$$

$$\rho_A(t_A, p_A, h_T) = \rho_{A,form}(t_A, p_A, h_T) + \delta\rho_{A,form}$$

where

$m$	mass contained or delivered by the volume instrument at actual conditions
$\delta m$	component arising because of influences not covered by $u(I_L)$ and $u(I_E)$
$u(I_L)$	uncertainty component of the weighing result of the recipient full of liquid
$u(I_E)$	uncertainty component of the weighing result of the empty recipient
$t_{W0}$	measured water temperature
$\delta t_W$	deviation arising from lack of homogeneity in the temperature within the weighed water mass
$t_{A0}$	measured air temperature
$\delta t_A$	deviation arising from air temperature inhomogeneity
$\delta t_S$	difference between water and artefact temperature
$\rho_{W,form}$	used water density formula (e.g. Tanaka's equation)
$\rho_{A,form}$	used air density formula (e.g. CIPM equation)
$\delta\rho_{W,form}$	estimated deviation from formula conditions (for water density)
$\delta\rho_{A,form}$	estimated deviation from formula conditions (for air density)
$\delta V_{op}$	auxiliary quantity to take into account possible errors or biases due to meniscus reading
$\delta V_{evap}$	auxiliary quantity to take into account possible errors or biases due to the evaporation

Note: all  $\delta x$  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:

$$V_{0, Average} = \sum_{k=1}^n \frac{V_{0,k}}{n}$$

## 7.2 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
- Water temperature
- Water density
- Air density
- Density of reference weights
- Cubic thermal expansion coefficient of the material of the instrument under calibration
- Operator effect
- Evaporation
- Measurement repeatability

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.

### 7.3 Standard uncertainty of each input quantity

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

#### 7.3.1 Mass

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

$$u(m) = \left[ u^2(I_L) + u^2(I_E) - 2r(I_L, I_E)u(I_L)u(I_E) + u^2(\delta m) \right]^{1/2} \quad (7)$$

The measurement uncertainty of  $I_E$  and  $I_L$  should be determined according to EURAMET Calibration Guide 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  $r(I_L, I_E)$ , may be negligible when compared with the other uncertainty components.

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

#### 7.3.2 Temperature (water and volume instrument)

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

$$u(t) = \left[ u^2(t_w) + u^2(\delta t_s) \right]^{1/2} \quad (8)$$

And,

$$u(t_w) = \left[ \left( \frac{U(ther)}{k} \right)^2 + u^2(res) + u^2(\delta t) + u^2(\delta t_w) \right]^{1/2} \quad (9)$$

Where:

$U(ther)$  - calibration expanded uncertainty of the liquid thermometer, in °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 covering factor will be  $k=2$ .

$u(res)$  – 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.

$u(\delta t_w)$  - 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 can be reduced to negligible values (10 to 20 mK) if the water is effectively 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  $u(\delta t_w) = (t_{\max} - t_{\min}) / \sqrt{12}$ , is an upper limit for the uncertainty of the mean temperature.

$u(\delta t_s)$  - 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  $u(\delta t_s)$  should be evaluated taking into account that the temperature of the artefact is most near to the temperature of the water rather the temperature of the air.

A conservative approach is to consider:  $u(\delta t_s) = \frac{|t_{A0} - t_w|}{2\sqrt{3}}$ , where  $t_{A0}$  and  $t_w$  are temperature of measured air temperature and temperature of the water respectively.

### 7.3.3 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  $u(\rho_{W,\text{form}}) = 4.5 \times 10^{-7}$  g/mL. This however is the uncertainty of the formulation alone, therefore, the uncertainty of the purity  $u(\delta \rho_w)$  and the contribution due to the temperature uncertainty of the water  $u(\rho_{W,t})$  (which depends on the expansion coefficient of the water  $\beta$ ) must be added.

$$u(\rho_w(t_w)) = \left[ u^2(\rho_{W,\text{form}}) + u^2(\rho_{W,t}) + u^2(\delta \rho_w) \right]^{1/2} \quad (10)$$

where

$$u(\rho_{W,t}) = u(t_w) \times \beta \times \rho_w(t_w)$$

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

$$\beta = (-0.1176 \times t^2 + 15.846 \times t - 62.677) \times 10^{-6} \text{ } ^\circ\text{C}^{-1} \quad (11)$$

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  $u(\delta\rho_W)$  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  $\mu\text{S/cm}$ , 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.

### 7.3.4 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 CIPM air density formula (4), the relative standard uncertainty is  $22 \times 10^{-6}$ .

For the CIPM simplified air density formula (5), the relative standard uncertainty due to the formula is  $u_{\text{form}} = 2.4 \times 10^{-4}$ .

If Spieweck's formula [9] is used, the air density relative standard uncertainty due to the formula is  $u_{\text{form}} = 4 \times 10^{-4}$ .

In addition to the uncertainty  $u_{\text{form}}$ , the uncertainties of the estimates for  $p_A$ ,  $h_r$  and  $t_A$  determine the total uncertainty  $u(\rho_A)$ .

$$u(\rho_A) = \rho_A \times \left[ \left( \frac{u_{p_A}(\rho_A)}{\rho_A} \times u(p_A) \right)^2 + \left( \frac{u_{t_A}(\rho_A)}{\rho_A} \times u(t_A) \right)^2 + \left( \frac{u_{h_r}(\rho_A)}{\rho_A} \times u(h_r) \right)^2 + \left( \frac{u_{\text{form}}(\rho_A)}{\rho_A} \right)^2 \right]^{1/2} \quad (12)$$

Note: the air that is actually 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 just 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 in the appropriate spot.

### 7.3.5 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.

### 7.3.6 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 % to 10 %.

### 7.3.7 Operator effect

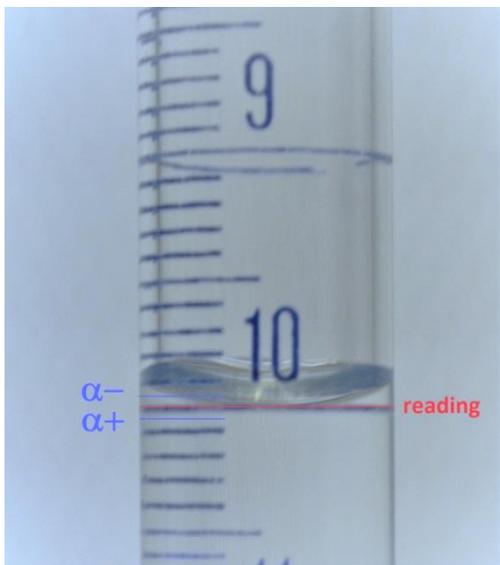
#### 7.3.7.1 Meniscus reading

The variability of meniscus settings and scale readings made by a single operator depends upon his/her 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  $\alpha$  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:  $\alpha = 0.1 \text{ mL}$

$\alpha + = 10.05 \text{ mL}$

$\alpha - = 9.95 \text{ mL}$

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

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

(rectangular)

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

(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:

$$u(\delta V_{\text{men}}) = u_p \times E \tag{13}$$

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 ( $u_p = 0.5 \ d$ ). 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.

### **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.

### 7.3.7.2 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 0.1 % of the measured volume.

### 7.3.8 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.

### 7.3.9 Measurement repeatability

Equation (14) is a possible expression for this Type A uncertainty component:

$$u(\delta V_{rep}) = \frac{s(V_o)}{\sqrt{n}} \quad (14)$$

Where:

$s(V_o)$  - standard deviation of a series of independent volume measurements, in mL

$n$  - number of measurements

Note: the value of volume that will be given as a result of  $n$  repeated measurements is the arithmetic mean of the  $n$  results, therefore its only Type A uncertainty component is the standard deviation of the mean,  $u(\delta V_{rep})$  as defined above.

## 7.4 Sensitivity coefficient of each input quantity

Defining the terms A, B and C by:

$$A = \frac{1}{\rho_W - \rho_A}; B = 1 - \left( \frac{\rho_A}{\rho_B} \right); C = 1 - \gamma(t - t_0) \text{ and with } m = I_L - I_E, \text{ equation (1) can be}$$

rewritten as:

$$V_0 = m \times A \times B \times C + \delta V_{op} + \delta V_{evap} + \delta V_{rep} \quad (15)$$

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, we now display the results of the calculation of the sensitivity coefficient based on the new formulation of equation (1) as equation (15).

#### 7.4.1 Mass

$$\left(\frac{\partial V_0}{\partial m}\right) = A \times B \times C \quad (16)$$

#### 7.4.2 Temperature

$$\left(\frac{\partial V_0}{\partial t}\right) = m \times A \times B \times (-\gamma) \quad (17)$$

#### 7.4.3 Water density

$$\left(\frac{\partial V_0}{\partial \rho_W}\right) = -m \times B \times C \times \frac{1}{(\rho_W - \rho_A)^2} = -m \times A^2 \times B \times C \quad (18)$$

#### 7.4.4 Air density

$$\left(\frac{\partial V_0}{\partial \rho_A}\right) = m \times C \times A \times \left[ \frac{1}{\rho_W - \rho_A} \times \left(1 - \frac{\rho_A}{\rho_B}\right) - \frac{1}{\rho_B} \right] = m \times A \times C \times (B \times A - 1/\rho_B) \quad (19)$$

#### 7.4.5 Density of the reference weights

$$\left(\frac{\partial V_0}{\partial \rho_B}\right) = m \times A \times C \times \frac{\rho_A}{\rho_B^2} \quad (20)$$

#### 7.4.6 Cubic thermal expansion coefficient of the material of the calibrated instrument

$$\left(\frac{\partial V_0}{\partial \gamma}\right) = m \times A \times B \times -(t - t_0) \quad (21)$$

#### 7.4.7 Operator effect

$$\frac{\partial V_0}{\partial \delta V_{op}} = 1 \quad (22)$$

#### 7.4.8 Evaporation

$$\frac{\partial V_0}{\partial \delta V_{evap}} = 1 \quad (23)$$

#### 7.4.9 Measurement repeatability

$$\frac{\partial V_0}{\partial \delta V_{rep}} = 1 \quad (24)$$

### 7.5 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:

$$u^2(V_0) = \sum_i \left( \frac{\partial V_0}{\partial x_i} \times u(x_i) \right)^2 \quad (25)$$

Using the expressions of the parts 7.3. and 7.4., the resultant combined standard uncertainty of the measurand is:

$$u(V_0) = \left[ \left( \frac{\partial V_0}{\partial m} \right)^2 u^2(m) + \left( \frac{\partial V_0}{\partial t} \right)^2 u^2(t) + \left( \frac{\partial V_0}{\partial \rho_W} \right)^2 u^2(\rho_W) + \left( \frac{\partial V_0}{\partial \rho_A} \right)^2 u^2(\rho_A) + \left( \frac{\partial V_0}{\partial \rho_B} \right)^2 u^2(\rho_B) + \left( \frac{\partial V_0}{\partial \gamma} \right)^2 u^2(\gamma) + u^2(\delta V_{op}) + u^2(\delta V_{evap}) + u^2(\delta V_{rep}) \right]^{\frac{1}{2}} \quad (26)$$

## 7.6 Evaluation of any existing covariances

Equation (25) and Equation (26) do not include any covariances terms. If some other correlations are identified they must be evaluated and introduced if influential.

## 7.7 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  $\nu_{eff}$ , can be estimated by means of the Welch-Satterthwaite formula:

$$\nu_{eff} = \frac{u_V^4}{\sum_{i=1}^N \frac{u_i^4}{\nu_i}} \quad (27)$$

$u_V$  – combined uncertainty of the determined volume

$u_i$  – standard uncertainty of each component

$\nu_i$  – degrees of freedom

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

## 7.8 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:

$$U = k \times u(V_0) \quad (28)$$

# 8 NUMERICAL EXAMPLE

## 8.1 Measurement problem

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

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

Input Quantity $X_i$	Value of the input quantity $x_i$
Mass	996.9499 g
Water temperature	20.50 °C
Water density	0.9981 g/mL
Air density	0.0012 g/mL
Density of the reference weights	7.96 g/mL
Cubic expansion coefficient of the flask material	$1 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$
Rectangular probability distribution for the meniscus reading	0
Measurement repeatability	0

After analysing the measurement problem (8.1.) and determining the volume of the flask according to the correct mathematical model, equation (1),  $V_{20} = 999.880 \text{ mL}$ , 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.

## 8.2 Determination of the standard uncertainty of each input quantity

### 8.2.1 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  $U(bal) = 0.007 \text{ g}$ , using a coverage factor of 2 and from the resolution of the weighing scale  $u(res) = 0.00029 \text{ g}$ , using a rectangular distribution, then:

$$u(I_L) = u(I_E) = \left[ u(bal)^2 + u(res)^2 \right]^{\frac{1}{2}} = \left[ \left( \frac{0.007 \text{ g}}{2} \right)^2 + \left( \frac{0.001 \text{ g}/2}{\sqrt{3}} \right)^2 \right]^{\frac{1}{2}} = 0.0034 \text{ g}$$

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

$$u(m) = \left[ u^2(I_L) + u^2(I_E) \right]^{\frac{1}{2}} = \left[ (0.0034 \text{ g})^2 + (0.0034 \text{ g})^2 \right]^{\frac{1}{2}} = 0.0048 \text{ g}$$

### 8.2.2 Temperature

The standard uncertainty of the water temperature was obtained from the value of the thermometer calibration  $U(ther) = 0.01$  °C, using a coverage factor of 2 and from the resolution of the thermometer  $u(res) = 0.005$  g, using a rectangular distribution. If we consider  $\delta t = 0$  and,  $\delta t_w = 0$ , equation (9) can be rewritten as:

$$u(t_w) = \left[ \left( \frac{U(ther)}{k} \right)^2 + u(res)^2 \right]^{1/2} = \left[ \left( \frac{0.01 \text{ °C}}{2} \right)^2 + \left( \frac{0.01 \text{ °C}/2}{\sqrt{3}} \right)^2 \right]^{1/2} = 0.006 \text{ °C}$$

Considering that the difference between air temperature and water temperature was 0.5 °C.

$$u(\delta t_s) = \frac{0.5 \text{ °C}}{2\sqrt{3}} = 0.144 \text{ °C}$$

Then,

$$u(t) = [u^2(t_w) + u^2(\delta t_s)]^{1/2} = [(0.006 \text{ °C})^2 + (0.144 \text{ °C})^2]^{1/2} = 0.144 \text{ °C}$$

### 8.2.3 Water density

The standard uncertainty of the water density was obtained from the value provided by equation (in 7.3.3), the uncertainty due to the temperature of the water

is  $u(\rho_{w,t}) = 1 \times 10^{-6}$  g/mL and the uncertainty due to the purity of the water

is  $u(\delta \rho_w) = 5 \times 10^{-6}$  g/mL, then:

$$u(\rho_w) = \left[ (4.5 \times 10^{-7} \text{ g/mL})^2 + (1.0 \times 10^{-6} \text{ g/mL})^2 + (5 \times 10^{-6} \text{ g/mL})^2 \right]^{1/2} = 5.1 \times 10^{-6} \text{ g/mL}$$

### 8.2.4 Air density

The relative standard uncertainty of the air density CIPM simplified formula is  $u_{form}(\rho_A) = 2.4 \times 10^{-4}$ . Considering the uncertainty values from the calibration of the pressure, temperature and humidity sensor, the uncertainty due to the temperature of the air is 0.1 °C, the uncertainty due to the barometric pressure is 10 Pa, the uncertainty due to the relative humidity is 1 %, then considering the sensitivity coefficients described in Appendix A of EURAMET Calibration Guide cg-18 [8]:

$$u(\rho_A) = 0.0012 \times \sqrt{\left( -4 \times 10^{-3} \times \frac{0.1 \text{ g/mL}}{2} \right)^2 + \left( 1 \times 10^{-5} \times \frac{10 \text{ g/mL}}{2} \right)^2 + \left( -9 \times 10^{-3} \times \frac{0.01 \text{ g/mL}}{2} \right)^2 + (2.4 \times 10^{-4} \text{ g/mL})^2} = 3.79 \times 10^{-7} \text{ g/mL}$$

### 8.2.5 Density of reference weights

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

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

### 8.2.6 Cubic thermal expansion coefficient of the material of the calibrated instrument

The thermal expansion coefficient of the flask is given by the manufacturer as  $\gamma = 1 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ , in the lack of a more informative statement, a rectangular probability distribution of  $\pm 5\%$  is assumed. The relevant standard uncertainty is therefore:

$$u(\gamma) = \frac{5 \times 10^{-7} \text{ }^\circ\text{C}^{-1}}{\sqrt{3}} = 2.89 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$$

### 8.2.7 Meniscus reading

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

$$u(\delta V_{men}) = \frac{0.036 \text{ mL}}{\sqrt{3}} = 0.021 \text{ mL}$$

### 8.2.8 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.

### 8.2.9 Measurement repeatability

Following equation (14), the type A uncertainty component can be determined by:

$$u(\delta V_{rep}) = \frac{s(V_o)}{\sqrt{n}} = \frac{0.034 \text{ mL}}{\sqrt{10}} = 0.011 \text{ mL}$$

## 8.3 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 (15).

### 8.3.1 Mass

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

### 8.3.2 Temperature of the standard in calibration

$$\left( \frac{\partial V_0}{\partial t} \right) = m \times A \times B \times (-\gamma) = -1 \times 10^{-2} \text{ mL/}^\circ\text{C}$$

### 8.3.3 Water density

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

### 8.3.4 Air density

$$\left(\frac{\partial V_0}{\partial \rho_A}\right) = m \times C \times A \times \left[ \frac{1}{\rho_w - \rho_A} \times \left(1 - \frac{\rho_A}{\rho_B}\right) - \frac{1}{\rho_B} \right] = m \times A \times C \times (B \times A - 1/\rho_B) = 877 \text{ (mL)}^2/\text{g}$$

### 8.3.5 Mass pieces density

$$\left(\frac{\partial V_0}{\partial \rho_B}\right) = m \times A \times C \times \frac{\rho_A}{\rho_B^2} = 1.87 \times 10^{-2} \text{ (mL)}^2/\text{g}$$

### 8.3.6 Cubic thermal expansion coefficient of the material of the flask

$$\left(\frac{\partial V_0}{\partial \gamma}\right) = m \times A \times B \times (-(t - t_0)) = -499.9^\circ\text{C} \cdot \text{mL}$$

### 8.3.7 Meniscus reading

$$\frac{\partial V_0}{\partial \delta V_{men}} = 1$$

## 8.4 Combined standard uncertainty of measurand

The combined uncertainty  $u(V_{20})$  is calculated from the equation (26). The individual terms are collected and substituted into this expression to obtain:

$$u(V_0) = \left[ \left(\frac{\partial V_0}{\partial m}\right)^2 u^2(m) + \left(\frac{\partial V_0}{\partial t}\right)^2 u^2(t) + \left(\frac{\partial V_0}{\partial \rho_w}\right)^2 u^2(\rho_w) + \left(\frac{\partial V_0}{\partial \rho_A}\right)^2 u^2(\rho_A) + \left(\frac{\partial V_0}{\partial \rho_B}\right)^2 u^2(\rho_B) + \left(\frac{\partial V_0}{\partial \gamma}\right)^2 u^2(\gamma) + u^2(\delta V_{men}) + u^2(\delta V_{rep}) \right]^{1/2} = 0.025 \text{ mL}$$

## 8.5 Evaluation of any existing covariances

The significant covariances were evaluated in section 7.3.1.

## 8.6 Choice of an appropriate coverage factor ( $k$ )

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

$$v_{eff}(V_{20}) = \frac{u_V^4}{\sum_{i=1}^N \frac{u_i^4}{v_i}} = \frac{u_{V_{20}}^4}{\frac{u^4(m)}{v(m)} + \frac{u^4(t)}{v(t)} + \frac{u^4(\rho_W)}{v(\rho_W)} + \frac{u^4(\rho_A)}{v(\rho_A)} + \frac{u^4(\rho_B)}{v(\rho_B)} + \frac{u^4(\gamma)}{v(\gamma)} + \frac{u^4(\delta V_{men})}{v(\delta V_{men})} + \frac{u^4(\delta V_{rep})}{v(\delta V_{rep})}}$$

$v_{eff}(V_{20}) = 242$ , which gives a coverage factor  $k = 2.01$  for a corresponding coverage probability of approximately 95 %.

## 8.7 Expanded uncertainty

The expanded uncertainty is deduced by:

$$U = k \times u(V_{20}) = 2.01 \times 0.025 = 0.050 \text{ mL}$$

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 $u(x_i)$	$c_i \equiv \frac{\partial f}{\partial x_i}$	$u_i \equiv c_i \times u(x_i)$ (mL)	Degrees of freedom
Mass	996.9499 g	$u(m)$	0.0048 g	1.00 mL/g	$4.82 \times 10^{-3}$	203
Temperature	20.50 °C	$u(t)$	0.144 °C	$-1 \times 10^{-2}$ mL/°C	$-1.44 \times 10^{-3}$	$\infty$
Water density	0.9981 g/mL	$u(\rho_W)$	$5.12 \times 10^{-6}$ g/mL	$-1000$ mL <sup>2</sup> /g	$-5.13 \times 10^{-3}$	$\infty$
Air density	0.0012 g/mL	$u(\rho_A)$	$3.79 \times 10^{-7}$ g/mL	877 mL <sup>2</sup> /g	$3.33 \times 10^{-4}$	$\infty$
Density of the reference weights	7.96 g/mL	$u(\rho_B)$	0.03 g/mL	$1.87 \times 10^{-2}$ mL <sup>2</sup> /g	$5.62 \times 10^{-4}$	$\infty$
Coefficient of thermal expansion from the flask material	$1 \times 10^{-5}$ °C <sup>-1</sup>	$u(\gamma)$	$2.89 \times 10^{-7}$ °C <sup>-1</sup>	$-499.9$ °CmL	$-1.44 \times 10^{-4}$	$\infty$
Meniscus reading	0	$u(\delta V_{men})$	0.021 mL	1	0.021	$\infty$
Measurement Repeatability	0	$u(\delta V_{rep})$	0.011 mL	1	0.011	9
					$u_c^2(V_{20}) = \sum u_i^2(V_{20}) = 6.27 \times 10^{-4}$ mL <sup>2</sup> $u_c(V_{20}) = 0.025$ mL $U(V_{20}) = 0.050$ mL $v_{eff}(V_{20}) = 242$ $k = 2.0$	

EURAMET e.V.  
Bundesallee 100  
38116 Braunschweig  
Germany

Phone: +49 531 592 1960  
Fax: +49 531 592 1969  
E-mail: [secretariat@euramet.org](mailto:secretariat@euramet.org)

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