

Guidelines on the determination of uncertainty in gravimetric volume calibration

EURAMET cg-19

Version 2.1 (03/2012)



Calibration Guide

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Purpose

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

Authorship

This document was developed by the EURAMET e.V., Technical Committee for Flow.

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Guidance Publications

This document gives guidance on measurement practices in the specified fields of measurements. By applying the recommendations presented in this document laboratories can produce calibration results that can be recognized and accepted throughout Europe. The approaches taken are not mandatory and are for the guidance of calibration laboratories. The document has been produced as a means of promoting a consistent approach to good measurement practice leading to and supporting laboratory accreditation.

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GUIDELINES ON THE DETERMINATION OF UNCERTAINTY IN GRAVIMETRIC VOLUME CALIBRATION

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1. Introduction

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. Laboratories must ensure that results obtained using these instruments are reliable. In order to reduce and identify 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 uncertainties as this must be displayed with the final result of the measurement to give the end use confidence in the measurement.

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

It should be noted that only "Type A" uncertainty components can be computed 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. All other components (the many "Type B" components) must be evaluated on the basis of all available sources of information, and through the operator's knowledge and expertise. 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.

2. Gravimetric method

The gravimetric method is the standard method used both by National Metrology Institutes (NMI's) and by accredited laboratories to calibrate volume instruments. The method consists on weighing the instrument under calibration when empty and again when full. The procedures adopted the use of the reference lines or marks to have the purpose to provide an exact measure of liquid volume and the draining or drying procedures should be followed carefully because they all affect the measurement. The difference obtained in the weighing measurements gives the mass of contained or delivered liquid. The liquid used is generally pure water (distilled, bi-distilled, or deionized) with a conductivity lower than 5 $\mu\text{S}/\text{cm}$ [2] 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 [3] 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
- ρ_W liquid density, in g/mL, at the calibration temperature t , in °C, according to equation (2)
- ρ_A air density, in g/mL, according to equation (3)
- ρ_B density of masses 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 liquid temperature 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 weighings. This ensures 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 formulations given in the literature. Batista and Paton [4] provide an overview of common formulations used in practice. It is however generally accepted that the formulation given by Tanaka [5] 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 °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 density of SMOW water under one atmosphere at this temperature. 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.

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 formulation based on this equation is given in ref. [4]. This provides an alternative to Tanaka and should be used if temperatures above 30 °C are used.

Where pure water is not available, the relative density of the water may be determined and the chosen formulation 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 [6]:

$$\rho_A / (10^{-3} \text{ kg} \cdot \text{m}^{-3}) = \left[3,483740 + 1,4446 \times (x_{CO_2} - 0,0004) \right] \times \frac{p}{ZT} \times (1 - 0,3780 \times x_V) \quad (3)$$

p ambient pressure, in Pa
 T thermodynamic temperature = $273,15 + t / ^\circ\text{C}$, in K
 x_V mole fraction of water vapour
 x_{CO_2} mole fraction of carbon dioxide in laboratory air
 Z compressibility factor

If the laboratory ambient conditions are within the limits given then Spieweck's [7] equation (4) can be used. The limits are: pressure between 940 hPa and 1080 hPa; temperature between 18 °C and 30 °C; humidity less than 80 %,

$$\rho_A = \frac{k_1 p_A + h_r (k_2 t_A + k_3)}{t_A + 273,15} \text{ g/mL} \quad (4)$$

Where :

t_A ambient temperature, in °C
 p_A ambient pressure, in hPa
 h_r relative air humidity, in %
 $k_1 = 3,4844 \times 10^{-4} \text{ } ^\circ\text{C/hPa}$
 $k_2 = -2,52 \times 10^{-6} \text{ g/mL}$
 $k_3 = 2,0582 \times 10^{-5} \text{ } ^\circ\text{C}$

3. Parameters that affect the 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 described.

3.1. 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 weights used to calibrate a electronic scale or with a balance.

3.2. Water density

Mass is converted into volume by determining the value of the calibration liquid density. This value can be obtained from the literature [4] or from direct measurements if pure water is not available.

3.3. Water temperature

The water temperature influences the determination of the water density; thus it should be carefully measured in each measurement. Methods for estimating the temperature of the water without changing the volume have to be established.

3.4. Ambient conditions

The ambient conditions mainly influence gravimetric measurement during the air density determination.

3.5. 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.

3.6. Operator

The operator can directly influence the measurement in the meniscus reading, in the filling and emptying procedure or in the handling of the equipment.

4. 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 programs exist which can avoid the error-prone manual calculation. Step 1 is the most important part in the whole GUM procedure.

5. Procedure for calculating uncertainty in gravimetric determination of volume

5.1. Mathematical expression of the volume V_0

$$V_0 = \frac{m}{\rho_W(t_W) - \rho_A(t_A, p_A, h_r)} \times \left(1 - \frac{\rho_A(t_A, p_A, h_r)}{\rho_B} \right) \times [1 - \gamma(t - t_0)] + \delta V_{\text{men}} + \delta V_{\text{evap}} + \delta V_{\text{rep}} \quad (5)$$

with

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

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

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

$$t = t_W + \delta t$$

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

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

where

| | |
|-----------------------|--|
| m | mass of filling at actual conditions |
| δm | component arising because of influences not covered by $u(I_L)$ and $u(I_E)$ |
| t_{W0} | measured water temperature |
| δt_W | deviation arising from water temperature inhomogeneity |
| t_{A0} | measured air temperature |
| δt_A | deviation arising from air temperature inhomogeneity |
| δt | difference between water and vessel temperature |
| $\rho_{W,form}$ | used water density formula (e.g. Tanaka's equation) |
| $\rho_{A,form}$ | used air density formula (e.g. Spiewek's 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) |
| δV_{men} | auxiliary quantity to treat the meniscus reading |
| δV_{evap} | auxiliary quantity to treat the evaporation |
| δV_{rep} | auxiliary quantity to treat the repeatability |

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

5.2. 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
Mass pieces density
Cubic thermal expansion coefficient of the material of the instrument under calibration
Meniscus reading
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 liquid) is not generally the same for repeated measurements, mainly owing to the variability of the quantity of water wetting 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.

5.3. Standard uncertainty of each input quantity

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

5.3.1. Mass

Equation (6) is a possible expression for this uncertainty component:

$$u(m) = \left[u^2(I_L) + u^2(I_E) - 2r(I_L, I_E)u(I_L)u(I_E) + u^2(\delta m) \right]^{1/2} \quad (6)$$

Note 1: Measurement uncertainty of I_L and I_E should include: mass standards used, balance resolution eccentricity, repeatability and linearity.

Note 2: Some correlations are present between the two readings of the balance (although they are obtained at different loads) as balance 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 , may be negligible when compared with the other uncertainty components.

5.3.2. Water temperature

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

$$u(t) = \left[\left(\frac{u(\text{ther})}{k} \right)^2 + u^2(\delta t) + u^2(\Delta t) \right]^{1/2} \quad (7)$$

Where:

$u(\text{ther})$ - measurements uncertainty of the 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 $k=2$.

δt - estimate of the uncertainty caused by possible drift and ageing of the temperature measuring system after its calibration.

Δt - estimate of the 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 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 $(t_{\max} - t_{\min})/\sqrt{12}$, is an upper limit for the uncertainty of the mean temperature.

5.3.3. Water density

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

For the formulation provided by Tanaka [5] has an estimated expanded uncertainty of 9×10^{-7} g/mL. This however is the uncertainty of the formulation and the uncertainty of the purity and temperature of the water used must be added.

If the information about the water preparation is insufficient or assuming 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, if the density of the working water is 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. This might range from a few ppm for highly pure water of known and controlled isotopic composition used for glassware calibration, to 20 ppm for lower quality distilled or de-ionised water from a reputable source used in proving tanks.

5.3.4. Air density

The uncertainty of the air density should be evaluated according to the chosen formula [6,7] and the input uncertainties.

For the CIPM air density formula (3), the relative standard uncertainty is 22×10^{-6} .

If Spieweck's formula (4) is used, the air density uncertainty may be expressed according to equation (8):

$$u(\rho_A) = \frac{5 \times 10^{-7}}{\sqrt{3}} \text{ g/mL} \quad (8)$$

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 % 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.

5.3.5. Density of mass pieces

The value presented in the calibration certificate of the set of masses, or of the analytical balance can be used. Alternatively the uncertainties corresponding to the used weight class according to OIML R 111-1 [8] can be used.

5.3.6. Cubic thermal expansion coefficient of the material of the calibrated instrument

The thermal expansion coefficients are dependent on knowledge of the actual material of the vessel 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 between 5 % and up to 10 %.

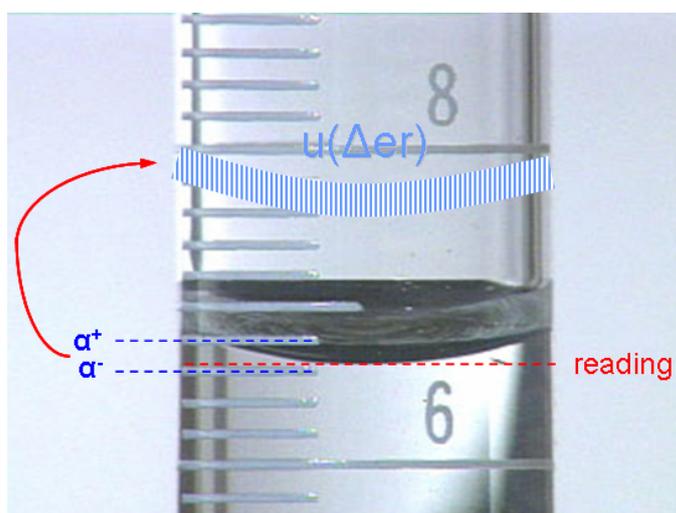
5.3.7. Meniscus reading

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 artifact) with reference to the ideal position defined by ref. [3] ("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 evaluating actual uncertainties occurring during the use of their own instrument) to estimate and compose a supplementary contribution if they think not to be able to approximate, the proper meniscus positioning within the same uncertainty limits.

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

5.3.7.1. Uncertainty in reading the position of a concave meniscus with respect to a graduated scale of a volumetric apparatus

In this case the uncertainty due to the meniscus could be estimated as the uncertainty in the volume determination due to the resolution (2α) of the scale of the volumetric apparatus. The usual practice is to assume a rectangular distribution and estimate the standard uncertainty as $\alpha/\sqrt{3}$. However, this approach could underestimate the actual technical skills 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 a triangular distribution instead, as shown in Fig. 1.



$$\alpha^+ = 6,8 \text{ mL}$$

$$\alpha^- = 6,6 \text{ mL}$$

$$\alpha = \frac{1}{2}(\alpha^+ - \alpha^-) \Rightarrow \alpha = 0,1 \text{ mL}$$

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

$$u(\Delta_{er}) = u(\delta V_{men}) = \frac{\alpha}{\sqrt{3}} = 0,058 \text{ mL}$$

(rectangular)

$$u(\Delta_{er}) = u(\delta V_{men}) = \frac{\alpha}{\sqrt{6}} = 0,041 \text{ mL}$$

(triangular)

Fig 1. Concave meniscus in a graduated volumetric device

5.3.7.2. Uncertainty in reading the position of a concave meniscus in a one-mark volumetric apparatus

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:

$$u(\delta V_{men}) = \frac{u_p \times E}{\sqrt{3}} \quad (9)$$

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 artifact may allow a standard uncertainty as low as 0,05 mm to be achieved.

5.3.7.3. 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.

5.3.8. 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.

5.3.9. Measurement repeatability

Equation (10) is a possible expression for this Type A uncertainty component:

$$u(\delta V_{rep}) = \frac{s(V_o)}{\sqrt{n}} \quad (10)$$

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. However, it is recommended that the number of measurements n and their standard deviation $s(V_o)$ be quoted in calibration reports or certificates, because if the user is going to make single, not averaged measurements, his Type A uncertainty contribution will not be $u(\delta V_{rep})$, but the standard deviation of the whole population of possible measurements, whose best estimate can be determined knowing n and $s(V_o)$.

5.4. Sensitivity coefficient of each input quantity

Defining the terms A, B and C by:

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

$$V_0 = m \times A \times B \times C + \delta V_{men} + \delta V_{evap} + \delta V_{rep} \quad (11)$$

The 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 (11).

5.4.1. Mass

$$\left(\frac{\partial V_0}{\partial m} \right) = A \times B \times C \quad (12)$$

5.4.2. Water temperature

$$\left(\frac{\partial V_0}{\partial t}\right) = m \times A \times B \times (-\gamma) \quad (13)$$

5.4.3. Water density

$$\left(\frac{\partial V_0}{\partial \rho_w}\right) = -m \times B \times C \times \frac{1}{(\rho_w - \rho_A)^2} = -m \times A^2 \times B \times C \quad (14)$$

5.4.4. Air density

$$\left(\frac{\partial V_0}{\partial \rho_A}\right) = m \times C \times A \times \left[\frac{1}{\rho_w - \rho_A} \times \left(1 - \frac{\rho_A}{\rho_B}\right) - \frac{1}{\rho_B} \right] = m \times A \times C \times (B \times A - 1/\rho_B) \quad (15)$$

5.4.5. Mass pieces density

$$\left(\frac{\partial V_0}{\partial \rho_B}\right) = m \times A \times C \times \frac{\rho_A}{\rho_B^2} \quad (16)$$

5.4.6. Cubic thermal expansion coefficient of the material of the calibrated instrument

$$\left(\frac{\partial V_0}{\partial \gamma}\right) = m \times A \times B \times (-(t - t_0)) \quad (17)$$

5.4.7. Meniscus reading

$$\frac{\partial V_0}{\partial \delta V_{men}} = 1 \quad (18)$$

5.4.8. Evaporation

$$\frac{\partial V_0}{\partial \delta V_{evap}} = 1 \quad (19)$$

5.4.9. Measurement repeatability

$$\frac{\partial V_0}{\partial \delta V_{rep}} = 1 \quad (20)$$

5.5. 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:

$$u^2(V_0) = \sum_i \left(\frac{\partial V_0}{\partial x_i} \times u(x_i) \right)^2 \quad (21)$$

Using the expressions of the parts 5.3. and 5.4., the resultant combined standard uncertainty of the measurand is:

$$u(V_0) = \left[\left(\frac{\partial V_0}{\partial m} \right)^2 u^2(m) + \left(\frac{\partial V_0}{\partial t} \right)^2 u^2(t) + \left(\frac{\partial V_0}{\partial \rho_w} \right)^2 u^2(\rho_w) + \left(\frac{\partial V_0}{\partial \rho_A} \right)^2 u^2(\rho_A) + \left(\frac{\partial V_0}{\partial \rho_B} \right)^2 u^2(\rho_B) + \left(\frac{\partial V_0}{\partial \gamma} \right)^2 u^2(\gamma) + u^2(\delta V_{men}) + u^2(\delta V_{evap}) + u^2(\delta V_{rep}) \right]^{\frac{1}{2}} \quad (22)$$

5.6. Evaluation of any existing covariances

Equation (21) and Equation (22) do not include any covariances terms. If some other correlations are identified they must be evaluated and introduced if influential.

5.7. 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, its number of degrees of freedom ν_{eff} , can be estimated by means of the Welch-Satterthwaite formula:

$$\nu_{eff} = \frac{u_V^4}{\sum_{i=1}^N \frac{u_i^4}{\nu_i}} \quad (23)$$

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).

5.8. 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:

$$U = k \times u(V_0) \quad (24)$$

6. Numerical example

6.1. Measurement problem

In order to apply numerical values to the uncertainty calculation procedure described above, a 1000 mL flask was calibrated. The data is summarized 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 |
|---|-------------------------------------|
| Mass | 996,9499 g |
| Water temperature | 20,5 °C |
| Water density | 0,9981 g/mL |
| Air density | 0,0012 g/mL |
| Density of the mass pieces | 7,96 g/mL |
| Coefficient of expansion from the flask material | $1 \times 10^{-5} / ^\circ\text{C}$ |
| Meniscus reading | 0,036 mL |
| Measurement repeatability | 0,011 mL |

After analyzing the measurement problem (6.1.) and determining the volume of the flask according to the correct mathematical model (equation 1), $V_{20} = 999,880$ mL, is necessary to determine the standard uncertainty of each input quantity, the sensitivity coefficients, the combined uncertainty, the degrees of freedom and corresponding k factor and finally the expanded uncertainty. The pertinent aspects of this example as discussed in this and the followings subclauses are summarized in table 2.

6.2. Determination of the standard uncertainty of each input quantity

6.2.1. 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 $U(bal) = 0,007$ g, using a coverage factor of 2 and from the resolution of the weighing scale $u(res) = 0,0005$ g, using a rectangular distribution, then:

$$u(I_L) = u(I_E) = \left[u(bal)^2 + u(res)^2 \right]^{\frac{1}{2}} = \left[\left(\frac{0,007}{2} \right)^2 + \left(\frac{0,001/\sqrt{2}}{\sqrt{3}} \right)^2 \right]^{\frac{1}{2}} = 0,00351 \text{ g}$$

If we consider that the correlations can be neglected and that $\delta m = 0$, equation 6 can be rewritten as:

$$u(m) = \left[u^2(I_L) + u^2(I_E) \right]^{\frac{1}{2}} = \left[0,00351^2 + 0,00351^2 \right]^{\frac{1}{2}} = 0,0048 \text{ g}$$

6.2.2. Water 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. If we consider $\delta t = 0$ and $\Delta t = 0$, equation 7 can be rewritten as:

$$u(t) = \left[\left(\frac{u(ther)}{k} \right)^2 \right]^{\frac{1}{2}} = \frac{0,01}{2} = 0,005 \text{ } ^\circ\text{C}$$

6.2.3. Water density

The standard uncertainty of the water temperature was obtained from the value provided by Tanaka = 9×10^{-7} g/mL, at which a coverage factor of 2 must be used and also from the uncertainty of the thermometer, with a value of $1,22 \times 10^{-6}$ g/mL, then:

$$u(\rho_W) = \left[\left(\frac{9 \times 10^{-7}}{2} \right)^2 + (1,22 \times 10^{-6})^2 \right]^{1/2} = 1,30 \times 10^{-6} \text{ g/mL}$$

6.2.4. Air density

The standard uncertainty of the water temperature was obtained from the value provided by Spieweck's:

$$u(\rho_A) = \frac{5 \times 10^{-7}}{\sqrt{3}} = 2,89 \times 10^{-7} \text{ g/mL}$$

6.2.5. Density of mass pieces

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:

$$u(\rho_B) = \frac{0,06}{2} = 0,03 \text{ g/mL}$$

6.2.6. Cubic thermal expansion coefficient of the material of the calibrated instrument

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

$$u(\gamma) = \frac{5 \times 10^{-7}}{\sqrt{3}} = 2,89 \times 10^{-7} / ^\circ\text{C}$$

6.2.7. Meniscus reading

The meniscus position was determined using optical aids and for this reason the standard uncertainty is 0,036 mL, with a rectangular distribution:

$$u(\text{men}) = \frac{0,036}{\sqrt{3}} = 0,021 \text{ mL}$$

6.2.8. 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.

6.2.9. Measurement repeatability

Following equation (10), the type A uncertainty component can be determined by:

$$u(\delta V_{rep}) = \frac{s(V_o)}{\sqrt{n}} = \frac{0,034}{\sqrt{10}} = 0,011 \text{ mL}$$

6.3. Sensitivity coefficient of each input quantity

For each input quantity, the results of the calculation of the sensitivity coefficient are display below, taken in to account equation 11.

6.3.1. Mass

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

6.3.2. Water temperature

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

6.3.3. Water density

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

6.3.4. Air density

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

6.3.5. Mass pieces density

$$\left(\frac{\partial V_0}{\partial \rho_B}\right) = m \times A \times C \times \frac{\rho_A}{\rho_B^2} = 1,87 \times 10^{-2} \text{ mL}^2/\text{g}$$

6.3.6. Cubic thermal expansion coefficient of the material of the flask

$$\left(\frac{\partial V_0}{\partial \gamma}\right) = m \times A \times B \times -(t - t_0) = -499,9 \text{ }^\circ\text{C} \cdot \text{mL}$$

6.3.7. Meniscus reading

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

6.3.8. Measurement repeatability

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

6.4. Combined standard uncertainty of measurand

The combined uncertainty $u(V_{20})$ is calculated from equation 22. The individual terms are collected and substituted into this expression to obtain:

$$u(V_0) = \left[\left(\frac{\partial V_0}{\partial m} \right)^2 u^2(m) + \left(\frac{\partial V_0}{\partial t} \right)^2 u^2(t) + \left(\frac{\partial V_0}{\partial \rho_w} \right)^2 u^2(\rho_w) + \left(\frac{\partial V_0}{\partial \rho_A} \right)^2 u^2(\rho_A) + \dots \right. \\ \left. \dots \left(\frac{\partial V_0}{\partial \rho_B} \right)^2 u^2(\rho_B) + \left(\frac{\partial V_0}{\partial \gamma} \right)^2 u^2(\gamma) + u^2(\delta V_{men}) + u^2(\delta V_{evap}) + u^2(\delta V_{rep}) \right]^{\frac{1}{2}} = 0,024 \text{ mL}$$

6.5. Evaluation of any existing covariances

There are no significant covariances.

6.6. Choice of an appropriate coverage factor (k)

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

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

$$\nu_{eff}(V_{20}) = \frac{3,61 \times 10^{-7}}{\frac{5,40 \times 10^{-10}}{203} + \frac{6,25 \times 10^{-18}}{50} + \frac{5,34 \times 10^{-12}}{3492} + \frac{4,10 \times 10^{-15}}{500000} + \frac{9,98 \times 10^{-14}}{500000} + \frac{4,30 \times 10^{-16}}{500000} + \frac{1,94 \times 10^{-7}}{500000} + \frac{1,46 \times 10^{-8}}{9}}$$

$\nu_{eff}(V_{20}) = 221$, Which corresponds to a coverage factor $k = 2$ and probability of approximately 95 %.

6.7. Expanded uncertainty

The expanded uncertainty is deduced by:

$$U = k \times u(V_{20}) = 2 \times 0,024 = 0,048 \text{ mL}$$

Table 2 – Summary for the standard uncertainty components

| Standard uncertainty component $u(x_i)$ | Source of uncertainty | Value of standard uncertainty $u(x_i)$ | $c_i \equiv \frac{\partial f}{\partial x_i}$ | $u_i(V_0) \equiv c_i u(x_i)$ (mL) | Degrees of freedom |
|---|--|--|--|-------------------------------------|--------------------|
| $u(m)$ | Mass | 0,0048 g | 1,00 | $4,82 \times 10^{-3}$ | 203 |
| $u(t)$ | Water temperature | 0,005 °C | -1×10^{-2} | $5,00 \times 10^{-5}$ | 50 |
| $u(\rho_W)$ | Water density | $1,30 \times 10^{-6}$ g / mL | -1003 | $1,30 \times 10^{-3}$ | 3492 |
| $u(\rho_A)$ | Air density | $2,89 \times 10^{-7}$ g / mL | 877 | $2,53 \times 10^{-4}$ | ∞ |
| $u(\rho_B)$ | Density of the mass pieces | 0,03 g / mL | $1,87 \times 10^{-2}$ | $5,62 \times 10^{-4}$ | ∞ |
| $u(\gamma)$ | Coefficient of expansion from the flask material | $2,89 \times 10^{-7}$ / °C | -499,9 | $1,44 \times 10^{-4}$ | ∞ |
| $u(\delta V_{men})$ | Meniscus reading | 0,021 mL | 1 | 0,021 | ∞ |
| $u(\delta V_{rep})$ | Measurement Repeatability | 0,011 mL | 1 | 0,011 | 9 |
| $u_c^2(V_{20}) = \sum u_i^2(V_{20}) = 6,01 \times 10^{-4}$ mL ² $u_c(V_{20}) = 0,024$ mL $\nu_{eff}(V_{20}) = 221$ | | | | | |

7. References

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