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Determination of uncertainty for volume measurements of a piston-operated volumetric apparatus using a gravimetric method

Détermination de l'incertitude de mesure pour les mesurages volumétriques des appareils volumétriques à piston au moyen de la méthode gravimétrique

Reference number
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Contents

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 48, *Laboratory equipment*.

This second edition cancels and replaces the first edition (ISO/TR 20461:2000), which has been technically revised and cancels ISO/TR 20461:2000/Cor 1:2008.

The main changes are as follows:

— the term “standard deviation of the mean delivered volume” has been replaced in this document by “repeatability” according to ISO/IEC Guide 99 ;

— a new uncertainty calculation example has been supplied;

— new uncertainty components have been added, namely, reproducibility, air cushion and resolution;

— a new Annex A concerning approaches for the estimation of uncertainty in use of a single delivered volume has been added;

— a new Annex B concerning volume correction due to pressure changes has been added.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The example given in this document is informative and supports the requirements found in ISO 8655-6:2022, 9.6 and ISO 8655-7:2022, 4.2, to perform an estimation of measurement uncertainty when calibrating POVA according to the measurement procedures described in these documents and the principles of ISO/IEC Guide 98-3.

The revision of this document coincides with a major revision of the ISO 8655 series in 2022, reflecting the state-of-the-art measurement procedures and approaches for the estimation of measurement uncertainty.

Determination of uncertainty for volume measurements of a piston-operated volumetric apparatus using a gravimetric method

1 Scope

This document gives detailed information regarding the evaluation of uncertainty for the gravimetric reference measurement procedure specified in ISO 8655-6[1] and the gravimetric procedure specified in ISO 8655-7:2022[1], Annex A, according to the ISO/IEC Guide 98-3[16].

This document also includes the determination of other uncertainty components related to the liquid delivery process of a piston-operated volumetric apparatus (POVA), e.g. repeatability and handling. Furthermore, it provides examples for the calculation and application of the uncertainty of the mean delivered volume and the uncertainty in use of a single delivered volume.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 8655-1, *Piston-operated volumetric apparatus — Part 1: Terminology, general requirements and user recommendations*

ISO/IEC Guide 2, *Standardization and related activities — General vocabulary*

ISO/IEC Guide 99, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 8655-1, ISO/IEC Guide 2 and ISO/IEC Guide 99 apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Modelling the measurement

In the gravimetric reference measurement procedure, a quantity of water is delivered by the instrument under calibration (POVA) into a vessel that is weighed on a balance. Ambient conditions are recorded so that the liquid density and air density can be determined and, consequently, the delivered volume can be calculated from this data.

Furthermore, the influence of possible evaporation and possible temperature difference of the POVA from the reference calibration temperature are taken into consideration as corrections in the mathematical model of the calibration.

The general formula for calculation of the volume at the reference temperature of 20 °C, V_{20} (at a reference temperature of 27 °C, V_{27}), from the balance indication of the delivered water as described in

ISO 4787[2] and the ISO 8655 series[1], is given by Formula (1). When a liquid other than water is used, Formula (1) is modified accordingly.

$$V_{ref} = (m_L - m_E + m_{evap}) \times \frac{1}{\rho_W - \rho_A} \times \left(1 - \frac{\rho_A}{\rho_B}\right) \times [1 - \gamma(t_W - t_{ref})] \quad (1)$$

where

V_{ref} is the calculated volume at the reference temperature, in ml;

m_L is the balance indication of the weighing vessel after water delivery, in g;

m_E is the balance indication of the weighing vessel before water delivery, in g (m_E = 0 in case the balance was tared with the weighing vessel);

m_{evap} is the estimated evaporated mass within a test cycle, in g;

ρ_A is the density of air, in g/ml, at the temperature, humidity and atmospheric pressure of the test, see Formula (3);

ρ_B is the density of the reference weights (typically 8 g/ml);

ρ_W is the density of water at the test temperature (in units of °C), in g/ml, calculated with the "Tanaka" Formula (4);

γ is the combined cubic thermal expansion coefficient of the POVA under test, in °C^{-1};

t_W is the temperature of the POVA, assumed to be equal to the temperature of the water used in the test, in °C;

NOTE The temperature of the POVA can be different from the temperature of the water, however the POVA temperature cannot be measured directly. The effect of a potential temperature difference can be taken into account in the uncertainty model.

t_{ref} is the reference temperature of the POVA (20 °C or 27 °C).

This model shows that the measured volume V_{ref} is a function of $m, t_W, \rho_A, \rho_B, \rho_W, \gamma$.

Formula (1) can be simplified by using the Z correction factor according to the following:

$$V_{ref} = m_i \times Z \times [1 - \gamma(t_W - t_{ref})] \quad (2)$$

where

m_i (i=1 to n) is each balance indication;

Z is a correction factor as a function of pressure and temperature that is given in ISO 8655-6:2022, Table A.1.

The simplified formula for the air density ρ_A, Formula (3), can be used at temperatures between 15 °C and 27 °C, barometric pressure between 600 hPa and 1 100 hPa, and relative humidity between 20 % and 80 %:

$$\rho_A = \frac{1}{1\ 000} \times \frac{0{,}348\ 48 \times p - 0{,}009 \times h_r \times e^{(0{,}061 \times t_A)}}{t_A + 273{,}15} \quad (3)$$

where

ρ_A is the air density, in g/ml;

t_A is the ambient temperature, in °C;

p is the barometric pressure, in hPa;

h_r is the relative air humidity, in %.

At other environmental conditions, Formula (3) is replaced with the calculations described in CIPM-2007[3].

Another commonly used formula for air density is described in Spieweck's work[4].

The density of pure water ρ_W is normally provided from formulae given in the literature. Formula (4) given by Tanaka[5] can be used:

$$\rho_W = a_5 \left[1 - \frac{(t_W + a_1)^2 (t_W + a_2)}{a_3 (t_W + a_4)} \right] \tag{4}$$

where

ρ_W is the density of water, in g/ml;

t_W is the water temperature, in °C;

a_1 −3,983 035 °C;

a_2 301,797 °C;

a_3 522 528,9 (°C)^2;

a_4 69,348 81 °C;

a_5 0,999 974 950 g/ml.

Atmospheric pressure corrections can also be applied to the volume delivered according to Annex B and Formula (B.1).

5 General procedure for the uncertainty calculation

The evaluation of measurement uncertainty in this document follows the ISO/IEC Guide 98-3. The method described has the following steps:

a) Expressing, in mathematical terms, the relationship between the measurand and its input quantities.

b) Determining the expected value of each input quantity.

c) Determining the standard uncertainty of each input quantity.

d) Determining the degree of freedom for each input quantity.

e) Determining all covariance between the input quantities.

f) Calculating the expected value for the measurand.

g) Calculating the sensitivity coefficient of each input quantity.

h) Calculating the combined standard uncertainty of the measurand.

i) Calculating the effective degrees of freedom of the combined standard uncertainty.

j) Choosing an appropriate coverage factor, k, to achieve the required confidence level.

k) Calculating the expanded uncertainty.

In this document, the uncertainty of the measurement associated with the volume is separated in three different clauses: the uncertainty components associated with the gravimetric measuring system, the uncertainty components associated with the device under test (POVA) and the uncertainty components associated with the liquid delivery process.

6 Standard uncertainty components associated with the measuring system (gravimetric measurement procedure)

6.1 General information on standard uncertainty components estimation

It is possible to experimentally estimate the standard uncertainty of measurement, $u(x)$, for a quantity x, by performing repeated measurements of x under identical experimental conditions. This is called a type A evaluation according to reference ISO/IEC Guide 98-3. The standard deviation of the obtained values is a measure of the repeatability of the measurement. The standard uncertainty associated with x can be the standard deviation (in the case where a single measurement of x is made), or the standard deviation of the mean equal to stdev(x)/sqrt(n) (in the case where x is the average of n readings).

See ISO/IEC Guide 98-3:2008, 4.2 for more information on type A evaluation of standard uncertainty.

As an alternative to repeated measurements, the uncertainty of measurement, $u(x)$, for a quantity x, can be estimated by other means. This is called a type B evaluation according to ISO/IEC Guide 98-3. For example, information can be obtained for that estimation by considering the manufacturer's specifications of the POVA (e.g. resolution, linearity, drift, temperature dependence, etc.).

Often the manufacturer's specifications are given in the form of an interval covering the measurement value, with no additional information regarding distribution or coverage. In those cases, the measurement is assumed to follow a uniform or rectangular distribution. This distribution is characterized by a constant probability inside the interval while the probability outside the interval is zero.

The interval can be used to give the variance of x in the form (type B evaluation according to ISO/IEC Guide 98-3) of:

$$u^2(x_i) = \frac{\left[\frac{1}{2}(a_{i+} - a_{i-})\right]^2}{3} = \frac{a_i^2}{3} \quad (5)$$

where a_{i-} and a_{i+} give the lower and the upper limits of the interval of the variable i.

a_i is half of this interval, typically the interval is denoted as $\pm a_i$ in this case. The standard uncertainty is given as the square root of the variance.

In addition to uniform rectangular, other distributions are also possible when preforming type B evaluations. See ISO/IEC Guide 98-3:2008, 4.3 for more information on type B evaluations of standard uncertainty.

The different expressions for the standard uncertainty of each input quantity related to the gravimetric reference measurement procedure are presented in the following formulas.

6.2 Standard uncertainty of weighing (balance indication)

The standard uncertainty $u(m)$ related to the balance indication (m) is calculated as follows:

$$u(m)=\left[u^2(m_L)+u^2(m_E)+u^2(\delta m)+u^2(m_{evap})\right]^{\frac{1}{2}} \tag{6}$$

where

$u(m_L)$ is the standard uncertainty associated with the balance indication of the weighing vessel after water delivery, in g;

$u(m_E)$ is the standard uncertainty associated with the balance indication of the weighing vessel before water delivery, in g;

$u(\delta m)$ is the drift of the balance, in g;

$u(m_{evap})$ is the standard uncertainty of the estimated mass of the evaporated quantity of water within a delivery cycle, in g. This is determined experimentally in each laboratory.

NOTE 1 The uncertainty of the balance indications can be estimated according to References [10] and [11] at the value corresponding to the selected volume.

The uncertainty of the balance indications can be taken from the balance calibration certificate if the expanded uncertainty in use is expressed. Otherwise, it can be calculated by using the uncertainty at calibration and including non-corrected errors, as well as possible drift and environmental effects to balance sensitivity.

The uncertainty calculation for the weighing is determined considering that the weighing vessel is not removed during the test. Additional uncertainties can arise if the vessel is removed from the balance.

NOTE 2 The correlations found in mass measurements are, in the case of this gravimetric measurement procedure, negligible.

6.3 Standard uncertainty of temperature

The standard uncertainty $u(t)$ related to the temperature (water and POVA), t, is calculated as follows:

$$u(t)=\left[u^2(t_W)+u^2(\delta t_s)\right]^{\frac{1}{2}} \tag{7}$$

where

$u(t_W)$ is the uncertainty of the temperature of the water;

$u(\delta t_s)$ is the estimation of the uncertainty caused by the variation between the water temperature and the temperature of the POVA;

and

$$u(t_W)=\left[\left(\frac{U_{ther}}{k}\right)^2+u^2(\text{res})+u^2(\delta t)\right]^{\frac{1}{2}} \tag{8}$$

where

U_{ther} is the calibration expanded uncertainty of the thermometer used to measure the liquid temperature, in °C;

k is the coverage factor (see Clause 11);

$u(\text{res})$ is the resolution of the used thermometer;

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

6.4 Standard uncertainty of water density

The standard uncertainty $u(\rho_W)$ related to the water density (ρ_W) is calculated as follows:

$$u(\rho_W) = \left[u^2(\rho_{W,form}) + u^2(\delta\rho_W) + u^2(\rho_{W,t})\right]^{\frac{1}{2}} \quad (9)$$

where

$u(\rho_{w,form})$ equals $4,5 \times 10^{-7}$, in g/ml[5];

$u(\delta\rho_W)$ is the uncertainty associated with the water purity, in g/ml;

NOTE If the quality of the water is of grade 3 according to ISO 3696, this uncertainty contribution can be considered negligible. More information on how to estimate this uncertainty contribution can be found in References [5] and [8].

$u(\rho_{W,t})$ is the contribution due to the uncertainty of the water temperature (which depends on the expansion coefficient of the water β), in g/ml.

$$u(\rho_{W,t}) = u(t_W) \times \beta \times \rho_W \quad (10)$$

The expansion coefficient of the water can be estimated as it is described in Reference [6].

$$\beta = \left(-0,117\,6 \times t^2 + 15,846 \times t - 62,677\right) \times 10^{-6} \ \ °\text{C}^{-1} \quad (11)$$

6.5 Standard uncertainty of air density

The standard uncertainty $u(\rho_A)$ related to the air density (ρ_A) is calculated according to OIML R 111-1:2004,[7] section C.6.3.6. as follows:

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

For the CIPM simplified air density Formula (2), the relative standard uncertainty due to the formula is $u_{form} = 2,4 \times 10^{-4}$.

6.6 Standard uncertainty of weights density

The standard uncertainty $u(\rho_B)$ related to the weights density (ρ_B) is obtained by the value presented in the calibration certificate of the set of reference weights used in the balance calibration. Alternatively, the uncertainties corresponding to the used weight class according to OIML R 111-1 can be used.

NOTE If EURAMET cg 18[11] is used for the calibration of the balance, the standard uncertainty $u(\rho_B)$ related to the weights density (ρ_B) is already taken into account and any further consideration is not needed.

6.7 Standard uncertainty related to air cushion effects

If applicable, the standard uncertainty related to the air cushion effect $u(\Delta V_{cush})$ depends on the size of the air cushion that is related to the lifting height in the pipette tip and can be calculated according to Formula (13) that is based on the information given in DKD R8-1 Guide, Clause 8.7[9]:

$$u(\Delta V_{cush}) = \left[\left(u(V\Delta p)\times c_{V\Delta p}\right)^2 + \left(u(V\Delta h_r)\times c_{V\Delta h_r}\right)^2 + \left(u(V\Delta t_s)\times c_{V\Delta t_s}\right)^2\right]^{\frac{1}{2}} \tag{13}$$

where

- $u(V\Delta p)$ is the estimation of uncertainty attributed to air pressure variation during the tests;
- $u(V\Delta h_r)$ is the estimation of uncertainty attributed to the humidity variation during the tests;
- $u(V\Delta t_s)$ is the estimation of uncertainty caused by variation between the water temperature, air temperature and temperature of the POVA under calibration;
- c_i are the sensitivity coefficients related to each uncertainty component.

NOTE The variations of each parameter are determined experimentally during the test.

The sensitivity coefficients (c_i) related to the air cushion effect from pressure, humidity and pressure can be derived from DKD R8-1 Guide[9].

7 Standard uncertainty components associated with the POVA

7.1 Standard uncertainty of cubic expansion coefficient

The standard uncertainty related to the cubic expansion coefficient γ is dependent on knowledge of the actual material of the device under test and on the source of data which provides the user with an appropriate value. Data from the literature or manufacturer can be used for the expansion coefficient and this value would be expected to have a relative standard uncertainty of 5 % to 10 % of the expansion coefficient value[8].

For devices with an air cushion, the thermal effects on the cubic expansion coefficient and the air cushion are entangled and are considered in tandem or determined experimentally. The details of this entanglement are beyond the scope of this document.

7.2 Standard uncertainty of resolution

The standard uncertainty related to the resolution can be determined according to Formula (14):

$$u(res) = \frac{\Delta res}{\sqrt{12}} \tag{14}$$

Where Δres is the actual or estimated resolution of the volume selection device of the apparatus.

NOTE The uncertainty related to the resolution of the POVA is included in the uncertainty budget when the measurements are dependent on the direct reading of the output volume, e.g. burette.

7.3 Standard uncertainty of setting

The setting of the volume in the POVA is evaluated and included in the uncertainty budget, if applicable.

NOTE For example, the setting uncertainty can be estimated using Formula (14).

8 Standard uncertainty components associated with the liquid delivery process

8.1 Repeatability (experimental standard deviation)

Formulae (6) to (13) allow the determination of the standard uncertainties associated with the gravimetric reference measurement procedure. To derive the standard uncertainty associated with the liquid delivery process, the experimental standard deviation is included. As the mean delivered volume is considered, the standard deviation, s_r, is divided by the square root of the number of repeated measurements n.

$$s_r(V_{\mathrm{ref}}) = \frac{s_r}{\sqrt{n}} \tag{15}$$

NOTE To avoid uncertainty underestimation, the repeatability contribution $s_r(V_{\mathrm{ref}}) = s_r$ can be used instead of Formula (15).

8.2 Reproducibility

It is important to include the uncertainty related to the reproducibility of V_{ref}. There are several methods to determine this uncertainty contribution:

— A laboratory can perform regular experimental studies;

— A laboratory can refer to studies conducted and published by third parties, e.g. EURAMET, DKD;

— If no such information is available,

  — A value for reproducibility of 0,1 % of the selected volume can be used for pipettes, see References [12] and [13]. For other POVA instruments different values are used. As no further information on the variation of individual measurements is taken into account, a rectangular distribution is suggested.

  — Alternatively, a standard uncertainty value for reproducibility as a fraction of the maximum permissible random error (MPRE) of the POVA can be used. In this case, a normal distribution is suggested due to the underlying random nature of this limit value.

9 Combined standard uncertainty of measurement associated with the volume V_{ref}

According to ISO/IEC Guide 98-3, the standard uncertainty of measurement associated with the volume V_{ref} is written as:

$$u^2(V_{ref}) = \sum_i c_i^2 \times u^2(x_i) \quad (16)$$

where

$u^2(x_i)$ are the standard uncertainties referred to the measurement of each input quantity which contributes to the final result (described by the model);

c_i^2 are the sensitivity coefficients giving the weight of each individual standard uncertainty.

The sensitivity coefficients are determined by calculating the partial derivatives of Formula (1), by numerical calculations, or by experiment.

10 Sensitivity coefficients

The sensitivity coefficients c_i in Formula (1) are calculated as partial derivatives using Formulae (17) to (22), where $Z = \frac{1}{\rho_W - \rho_A} \times \left(1 - \frac{\rho_A}{\rho_B}\right)$

The sensitivity coefficient c_m related to the balance indication m is calculated as follows:

$$c_m = \left(\frac{\partial V_{ref}}{\partial m}\right) = Z \times [1 - \gamma(t_W - t_{ref})] \text{ in ml/g} \quad (17)$$

The sensitivity coefficient c_{t_w} related to the temperature t_w of the water is calculated as follows:

$$c_{t_w} = \left(\frac{\partial V_{ref}}{\partial t_W}\right) = m \times Z \times (-\gamma) \text{ in ml/°C} \quad (18)$$

The sensitivity coefficient c_{ρ_W} related to the water density ρ_W is calculated as follows:

$$c_{\rho_W} = \left(\frac{\partial V_{ref}}{\partial \rho_W}\right) = -m \times \left(1 - \frac{\rho_A}{\rho_B}\right) \times [1 - \gamma(t_W - t_{ref})] \times \frac{1}{(\rho_W - \rho_A)^2} \text{ in ml}^2\text{/g} \quad (19)$$

The sensitivity coefficient c_{ρ_A} related to the density of air ρ_A is calculated as follows:

$$c_{\rho_A} = \left(\frac{\partial V_{ref}}{\partial \rho_A}\right) = m \times [1 - \gamma(t_W - t_{ref})] \times \frac{1}{\rho_W - \rho_A} \times \left[Z - \frac{1}{\rho_B}\right] \text{ in ml}^2\text{/g} \quad (20)$$

The sensitivity coefficient c_γ related to the cubic expansion coefficient γ of the piston-operated volumetric apparatus is calculated as follows:

$$c_\gamma = \left(\frac{\partial V_{ref}}{\partial \gamma}\right) = m \times Z \times [-(t_W - t_{ref})] \text{ in °C ml} \quad (21)$$

It is emphasized that γ is not a well-defined value for a compound system.

The sensitivity coefficient c_{ρ_B} related to the density of the standard weights ρ_B is calculated as follows:

$$c_{\rho_B} = \left(\frac{\partial V_{ref}}{\partial \rho_B}\right) = m \times \frac{1}{\rho_W - \rho_A} \times [1 - \gamma(t_W - t_{ref})] \times \frac{\rho_A}{\rho_B{}^2} \text{ in ml}^2/\text{g} \quad (22)$$

The sensitivity coefficient for the standard deviation of the repeatability, the reproducibility and the resolution have the value of 1 because it is in the same unit as the measurements. In this case, $\left(c_{V_{ref}} = \frac{\partial V_{ref}}{\partial V_{ref}}\right)$.

11 Choice of an appropriate coverage factor (k)

In order to calculate an appropriate coverage factor (k) for a 95 % confidence level (see ISO/IEC Guide 98-3:2008, Annex G) the effective degrees of freedom ν_{eff}, are estimated by means of the Welch-Satterthwaite formula:

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

where

u_V is the combined uncertainty of the determined volume;

u_i is the standard uncertainty of each component;

ν_i are the degrees of freedom for each component.

For 10 or more measurements, k can be calculated or k = 2 can be used if the individual standard uncertainty values have a similar weight in the combined uncertainty. For less than 10 measurements, k is calculated.

12 Expanded uncertainty of measurement associated with the volume V_{ref}

The expanded uncertainty of the volume $U(V_{ref})$ is expressed as:

$$U(V_{ref}) = k \times u(V_{ref}) \quad (24)$$

where the standard uncertainty is multiplied by the coverage factor k.

For example, the result of the measurement is given as:

$$V_{ref} \pm U(V_{ref}) \quad (25)$$

13 Example for determining the uncertainty of the volume measurement of POVA

13.1 Measurement conditions

The measurement conditions are as follows:

— tenfold measurement of a selected volume, V_s, of 100 µl of water, delivered by a piston-operated pipette;

— balance: 220 g balance with a resolution of 10 µg;

— reference temperature of V_{ref} is 20 °C

— mean volume: $V_{ref} = 99{,}56\,\mu l$;

— random error of measurement (experimental standard deviation): $s_r = 0{,}19\,\mu l$;

— experimental standard deviation of the mean: $s_r(V_{ref}) = s_r / \sqrt{n} = 0{,}19\,\mu l / \sqrt{10} = 0{,}06\,\mu l$;

— systematic error of measurement: $V_{ref} - V_s = 99{,}56\,\mu l - 100\,\mu l = -0{,}44\,\mu l$.

The determination of the uncertainty for these conditions is given in Table 1.

Table 1 — Determination of uncertainty of POVA

Uncertainty component	Estimation average value	Unit	Symbol	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient[a] c_i	Uncertainty (µl)	ν_{eff}
	Formula (1)						$c_i \times u(x_i)$	
Measuring system								
Weighing	99,29	mg	m	normal	$1,898 \times 10^{-2}$	1	$1,898 \times 10^{-2}$	234
Water temperature	22,67	°C	t_W	rectangular	$1,601 \times 10^{-2}$	$-2,391 \times 10^{-2}$	$-3,828 \times 10^{-4}$	∞
Water density	0,997 6	mg/µl	ρ_W	rectangular	$5,000 \times 10^{-5}$	−99,92	$-4,996 \times 10^{-3}$	∞
Air density	0,001 2	mg/µl	ρ_A	rectangular	$1,095 \times 10^{-6}$	87,41	$9,570 \times 10^{-5}$	∞
Weights density[b]	8	mg/µl	ρ_B	N/A				
Air cushion effects		µl	ΔV_{cush}	rectangular	$6,209 \times 10^{-3}$	1	$6,209 \times 10^{-3}$	∞
Device under test (POVA)								
Cubic thermal expansion coefficient	$2,4 \times 10^{-4}$	1/°C	γ	rectangular	$6,928 \times 10^{-6}$	$-2,663 \times 10^{2}$	$-1,845 \times 10^{-3}$	∞
Resolution	N/A		Δres					
Liquid delivery process								
Reproducibility		µl	δV_{rep}	rectangular	$5,732 \times 10^{-2}$	1	$5,732 \times 10^{-2}$	∞
Repeatability (experimental standard deviation of the mean)		µl	$s_r(V_{ref})$	normal	$6,039 \times 10^{-2}$	1	$6,039 \times 10^{-2}$	9
Standard uncertainty of the mean delivered volume (combined uncertainty)		µl	$u(V_{ref})$				0,086	
ν_{eff}							37	
k[c]							2,07	
Expanded uncertainty of the mean delivered volume		µl	$U(V_{ref})$				0,18	

[a] For calculations and units see Formulae (17) to (22). For this case, the units replace g per mg and ml for µl in the applicable formulae.

[b] If the balance is calibrated following EURAMET cg 18 [11] this uncertainty component is already included in the weighing contribution.

[c] This value is obtained based on the degrees of freedom, Formula (23).

13.2 Results

13.2.1 Calculations

The standard uncertainty of the mean delivered volume is

$$u(V_{\text{ref}}) = 0{,}086\,\mu\text{l}.$$

The expanded uncertainty of the mean delivered volume is determined by

$$U(V_{\text{ref}}) = 0{,}086\ \mu\text{l} \times 2{,}07 = 0{,}18\ \mu\text{l}.$$

The result of measurement is given by

$$V_{\text{ref}} = 99{,}56\,\mu\text{l} \pm 0{,}18\,\mu\text{l}\,(k = 2{,}07).$$

13.2.2 Uncertainty in use and corrections for pressure changes

The uncertainty in use of a single delivered volume is discussed in Annex A. The volume correction due to changes in atmospheric pressure is discussed in Annex B.

13.2.3 General remarks

Some of the numerical values of the sensitivity coefficients are volume dependent. It is not possible to use the values given in the example for other volumes.

13.2.4 Note on the conformity of the ISO 8655 series with ISO/IEC Guide 98-3

The random error of measurement is equivalent to the term "experimental standard deviation" used in ISO/IEC Guide 98-3. There is no direct equivalent to systematic error of measurement in ISO/IEC Guide 98-3. But a simple way to be in conformity with ISO/IEC Guide 98-3 is to expand the model defining a new quantity $V_{\text{d}} = V_{\text{s}} - V_{\text{ref}}$ where V_{s} is the selected volume of the piston-operated volumetric apparatus. In this case, the result of the measurement V_{d} is opposite in sign to the systematic error of measurement defined in ISO 8655-6. The measurement uncertainty is unchanged as V_{s} has a zero uncertainty.

The systematic error of measurement does not influence the measurement uncertainty of the volume V_{ref} measured with the gravimetric measuring system. It is the result of a measurement made using the gravimetric measuring system and can be referred to the piston-operated volumetric apparatus. It is a measure characterizing the volume delivered by the piston-operated volumetric apparatus.

More information on uncertainty calculation regarding the gravimetric method can be found in EURAMET cg 19[8].

Annex A
(informative)

Approaches for the estimation of uncertainty in use of a single delivered volume

A.1 General

For POVA delivering volumes in the laboratory in daily use the uncertainty in use of a single delivered volume can be estimated. This uncertainty is larger than the uncertainty of the mean delivered volume $u(V_{ref})$ described in 13.2 and differs in two major ways:

a) Only a single delivered volume is considered, so that the experimental standard deviation (s_r) is used and not $s_r / \sqrt{n}$.

b) The systematic error is added to the uncertainty, taking into account that many POVA users do not correct the measurement for its systematic error in daily use.

The approaches in this annex are practical simplifications and are not covered in the uncertainty concept of ISO/IEC Guide 98-3. It is good practice to determine whether these approaches cover the laboratory's specific application.

Numerical values used in the calculations in A.2 and A.3 are taken from 13.1 for purposes of illustration. When applying this concept, calculations are based on numerical values from data acquired in the laboratory where the POVA is used.

A.2 Uncertainty for a single delivered volume from a test data set

$$u_{sd}(V_{ref}) = \left(0{,}061^2 + 0{,}19^2\right)^{1/2} \ \mu l = 0{,}20 \ \mu l$$

The same uncertainty of the gravimetric measurement procedure is used as in 13.2.1. However, s_r is used instead of $s_r / \sqrt{10}$, because only a single delivered volume is considered.

The expanded uncertainty for a single delivered volume is calculated using the following Formula (A.1):

$$U_{sd}(V_{ref}) = k \times u_{sd}(V_{ref}) \quad \text{(A.1)}$$

In this example $U_{sd}(V_{ref}) = 2{,}07 \times 0{,}20 \ \mu l = 0{,}41 \ \mu l$

NOTE Factor k is taken to be the same as for Table 1.

A.3 Uncertainty in use of a single delivered volume

A.3.1 Calculations

According to ISO/IEC Guide 98-3, a measurement can be corrected for known systematic errors. This is not always practical for the user of the POVA in daily use. Thus, the uncertainty in use of a single delivered volume includes both the systematic and the random errors of the deliveries.

Furthermore, the uncertainty in use of a single delivered volume is useful when assessing the accuracy of a delivered volume for a particular application and when evaluating POVA by routine testing. For

