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## Determination of uncertainty for volume measurements made using the gravimetric method

*Détermination de l'incertitude de mesure pour les mesurages  
volumétriques effectués au moyen de la méthode gravimétrique*



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## Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

Attention is drawn to the possibility that some of the elements of ISO/TR 20461 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TR 20461 was prepared by Technical Committee ISO/TC 48, *Laboratory glassware and related apparatus*, Subcommittee SC 1, *Volumetric instruments*.

# Determination of uncertainty for volume measurements made using the gravimetric method

## 1 Scope

This Technical Report gives the detailed evaluation of uncertainty for volume measurements according to the *Guide to the Expression of Uncertainty in Measurement* (GUM) [1]. It uses the gravimetric method specified in ISO 8655-6 [2] as the reference method for calibrating piston-operated volumetric apparatus. It has been arranged in paragraphs to facilitate direct access to different aspects of this kind of evaluation as follows:

- modelling the measurement by describing the physical equations necessary to calculate the volume using the gravimetric method of measurement;
- determination of the standard uncertainty of measurement associated with the volume  $V_{20}$  by describing the calculation procedure according to the GUM;
- determination of the sensitivity coefficients with an example of the calculation of all sensitivity coefficients by using complete equations, approximations of equations and by giving numerical values for standard conditions;
- determination of the standard uncertainty associated with the volume delivered by a piston-operated volumetric apparatus giving the combination of the standard uncertainty associated with the volume  $V_{20}$  measured using the gravimetric measuring system and the experimental standard deviation associated with the volume delivered by the apparatus;
- determination of the standard uncertainties of measurement with a brief insight into the calculation of uncertainties of measuring devices according to GUM;
- determination of the expanded uncertainty of measurement associated with volume  $V_{20}$ ;
- example of the determination of the uncertainty for volume measurements.

## 2 Modelling the measurement

The equation for the volume  $V_{20}$  of the delivered water at 20 °C is given by

$$V_{20} = m \times Z \times Y \quad (1)$$

with

$$m = m_2 - m_1 - m_E \quad (2)$$

where

$m$  is the balance reading of delivered water;

$m_1$  is the balance reading of the weighing vessel before delivery of the measured volume of water;

$m_2$  is the balance reading of the weighing vessel after delivery of the measured volume of water;

$m_E$  is the balance reading of the mass loss due to evaporation of liquid during the measurement;

$Z$  is the combined factor for buoyancy correction and conversion from mass to volume;

$Y$  is the thermal expansion correction factor of the delivering device.

Equation (1) combines the measurement results yielded by the balance ( $m$ ), air and liquid densities yielded by measurements of air and liquid temperatures, air pressure and relative humidity of air in conjunction with tables or equations for the factor ( $Z$ ), and parameters of the delivering device ( $Y$ ).

$Z$  is given by

$$Z = \frac{1}{\rho_w} \times \frac{1 - \frac{\rho_a}{\rho_b}}{1 - \frac{\rho_a}{\rho_w}} = \frac{1}{\rho_b} \times \frac{\rho_b - \rho_a}{\rho_w - \rho_a} \quad (3)$$

where

$\rho_w$  is the density of water;

$\rho_a$  is the density of air;

$\rho_b$  is the density of the standard weight used to calibrate the balance [according to OIML (Organisation Internationale de Métrologie Légale),  $\rho_b = 8\,000\text{ kg/m}^3$  for steel weights].

The density of water  $\rho_w$  (in  $\text{kg/m}^3$ ) is given by an equation [3] which is a very useful approximation of the equation of Kell [4],[5] in the temperature range  $5\text{ °C}$  to  $40\text{ °C}$ . The relative deviation between this equation and the original equation of Kell (given in reference [5] in terms of the ITS-90 temperature scale and valid for temperatures between  $0\text{ °C}$  and  $150\text{ °C}$ ) is less than  $10^{-6}$  in the temperature range  $5\text{ °C}$  to  $40\text{ °C}$ .

$$\rho_w = \sum_{i=0}^4 a_i t_w^i \quad (4)$$

where

$t_w$  is the water temperature in degrees Celsius;

with the constants (ITS-90 temperature scale):

$a_0$  is equal to  $999,853\,08\text{ kg/m}^3$ ;

$a_1$  is equal to  $6,326\,93 \times 10^{-2}\text{ °C}^{-1}\text{ kg/m}^3$ ;

$a_2$  is equal to  $8,523\,829 \times 10^{-3}\text{ °C}^{-2}\text{ kg/m}^3$ ;

$a_3$  is equal to  $6,943\,248 \times 10^{-5}\text{ °C}^{-3}\text{ kg/m}^3$ ;

$a_4$  is equal to  $3,821\,216 \times 10^{-7}\text{ °C}^{-4}\text{ kg/m}^3$ .

Any additional corrections for the pressure dependence and gas saturation of the water density are negligible as they are very small.

The density of air  $\rho_a$  (in kg/m<sup>3</sup>) is given by [5]:

$$\rho_a = \frac{k_1 p_a + \varphi (k_2 t_a + k_3)}{t_a + t_{a0}} \quad (5)$$

where

$t_{a0}$  is equal to 273,15 °C;

$p_a$  is the pressure, expressed in hectopascals (hPa);

$\varphi$  is the relative humidity, expressed as a percentage;

$t_a$  is the air temperature, expressed in degrees Celsius;

with the constants (ITS-90 temperature scale):

$k_1$  is equal to 0,348 44 (kg/m<sup>3</sup>) °C/hPa;

$k_2$  is equal to -0,002 52 kg/m<sup>3</sup>;

$k_3$  is equal to 0,020 582 (kg/m<sup>3</sup>) °C.

The correction for the thermal expansion of the delivering device is given by

$$Y = 1 - \alpha_c (t_d - t_{d20}) \quad (6)$$

where

$\alpha_c$  is the cubic expansion coefficient in °C<sup>-1</sup>;

$t_d$  is the device temperature in degrees Celsius;

$t_{d20}$  is equal to 20 °C.

The temperatures  $t_w$ ,  $t_a$ , and  $t_d$  are assumed to be uncorrelated, as the actual values of  $t_w$  and  $t_d$  do not only depend on  $t_a$ , but also strongly depend on the handling by the user. Considerable effects of evaporation-cooling and hand-warming when using handheld apparatus are to be taken into account. The resulting temperature differences are often larger than the uncertainty in the temperature measurement.

Equations (1) to (6) show that one may write:

$$V_{20} = \frac{m}{\rho_b} \cdot \frac{\rho_b - \rho_a}{\rho_w - \rho_a} \cdot [1 - \alpha_c (t_d - t_{d20})] \quad (7)$$

This model shows that the measured volume  $V_{20}$  is a function of  $m$ ,  $t_w$ ,  $t_a$ ,  $p_a$ ,  $\varphi$ ,  $\alpha_c$ ,  $t_d$ , and some constants.

$$V_{20} = F(x_i) = F(m, t_w, t_a, p_a, \varphi, \alpha_c, t_d; \text{constants}) \quad (8)$$

### 3 Standard uncertainty of measurement associated with the volume $V_{20}$

According to the GUM the standard uncertainty of measurement associated with the value  $V_{20}$  may be written as:

$$u^2(V_{20}) = \sum_i c_i^2 \times u^2(x_i) = \sum_i \left( \frac{\partial F}{\partial x_i} \right)^2 \times u^2(x_i) \quad (9)$$

$$u^2(V_{20}) = \left( \frac{\partial F}{\partial m} \right)^2 \times u^2(m) + \left( \frac{\partial F}{\partial t_w} \right)^2 \times u^2(t_w) + \left( \frac{\partial F}{\partial t_a} \right)^2 \times u^2(t_a) + \left( \frac{\partial F}{\partial p_a} \right)^2 \times u^2(p_a) + \dots \quad (10)$$

where

$u^2(x_i)$  are the standard uncertainties referred to the measurement of each 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 may be determined by calculating the partial derivatives as indicated in equation (9), by numerical calculations, or by experiment.

As the uncertainties of the constants [equation (8)] and the uncertainties of equations (4) and (5) for  $\rho_w$  and  $\rho_a$  are very small compared to other uncertainties, they may be neglected in the evaluation of uncertainty.

### 4 Sensitivity coefficients

The evaluation of the uncertainty of measurement does not require such exact values and exact solutions of the mathematical model for the measurement, as the determination of the volume  $V_{20}$  itself. Approximations are tolerable, but they have to be used only for this uncertainty evaluation.

In the following the approximations  $\rho_w - \rho_a \approx \rho_w$ ,  $\rho_b - \rho_a \approx \rho_b$ ,  $\rho_w \approx 1000 \text{ kg/m}^3$ ,  $1 - \alpha_c(t_d - t_{d20}) \approx 1$ , and  $\rho_b - \rho_w \approx \rho_b$  are used without special notation. Keep in mind that the first approximations are of the order  $10^{-3}$  or less, whereas the last approximation is of the order  $10^{-1}$ . This last approximation is justified as it is affecting only the air buoyancy correction.

The sensitivity coefficients  $c_i$  in equation (9) are calculated as partial derivatives using equations (11) to (29).

The sensitivity coefficient  $c_w$  related to the balance reading  $m$  is calculated as follows:

$$c_w = \frac{\partial F}{\partial m} = \frac{V_{20}}{m} \quad (11)$$

$$c_w = \frac{\partial F}{\partial m} \approx \rho_w \quad (12)$$

$$c_w = \frac{\partial F}{\partial m} \approx 10^{-3} \frac{\text{m}^3}{\text{kg}} = 1 \frac{\text{nl}}{\mu\text{g}} \quad (13)$$

The sensitivity coefficient  $c_{\alpha_c}$  related to the cubic expansion coefficient  $\alpha_c$  of the piston-operated volumetric apparatus is calculated as follows:

$$c_{\alpha_c} = \frac{\partial F}{\partial \alpha_c} = -\frac{m}{\rho_b} \times \frac{\rho_b - \rho_a}{\rho_w - \rho_a} \times (t_d - t_{d20}) \quad (14)$$

$$c_{\alpha_c} = \frac{\partial F}{\partial \alpha_c} \approx -\frac{m}{\rho_w} \times (t_d - t_{d20}) \quad (15)$$

$$c_{\alpha_c} = \frac{\partial F}{\partial \alpha_c} \approx -10^{-3} \left( \frac{\text{kg}}{\text{m}^3} \text{K} \right)^{-1} \times m \times (t_d - 20 \text{ } ^\circ\text{C}) \quad (16)$$

It should be emphasized that  $\alpha_c$  is not a well defined value for a compound system.

The sensitivity coefficient  $c_{t_d}$  related to the temperature  $t_d$  of the piston-operated volumetric apparatus is calculated as follows:

$$c_{t_d} = \frac{\partial F}{\partial t_d} = -\frac{m}{\rho_b} \times \frac{\rho_b - \rho_a}{\rho_w - \rho_a} \times \alpha_c \quad (17)$$

$$c_{t_d} = \frac{\partial F}{\partial t_d} \approx -\frac{m}{\rho_w} \times \alpha_c \quad (18)$$

If  $\alpha_c = 10^{-5} \text{ K}^{-1}$  is used:

$$c_{t_d} = \frac{\partial F}{\partial t_d} \approx 10^{-8} \left( \frac{\text{kg}}{\text{m}^3} \text{K} \right)^{-1} \times m \quad (19)$$

It should be emphasized that the temperature  $t_d$  of the piston-operated volumetric apparatus is neither spatially nor temporally constant because of hand-warming at the middle and the top, and evaporation-cooling at the bottom of the apparatus.

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

$$c_{t_w} = \frac{\partial F}{\partial t_w} = -\frac{m}{\rho_b} \times \frac{1 - \alpha_c(t_d - t_{d20})}{(\rho_w - \rho_a)^2} \times (\rho_b - \rho_a) \times \left( \sum_{i=1}^4 i a_i t_w^{i-1} \right) \quad (20)$$

$$c_{t_w} = \frac{\partial F}{\partial t_w} \approx -\frac{m}{\rho_w^2} \times \frac{\partial \rho_w}{\partial t_w} = -\frac{m}{\rho_w^2} \times \left( \sum_{i=1}^4 i a_i t_w^{i-1} \right) \quad (21)$$

It is possible to use the expression  $\frac{\partial \rho_w}{\partial t_w} = -2,1 \times 10^{-4} \text{ K}^{-1} \times \rho_w$  instead of the sum given in equation (21) in the temperature range of 19 °C to 21 °C with sufficient accuracy.

$$c_{t_w} = \frac{\partial F}{\partial t_w} \approx \frac{m}{\rho_w} \times 2,1 \times 10^{-4} \text{ K}^{-1} = 2,1 \times 10^{-7} \left( \frac{\text{kg}}{\text{m}^3} \text{K} \right)^{-1} \times m \quad (22)$$

It should be emphasized that  $t_w$  may also be affected by evaporation-cooling as by hand-warming.

The sensitivity coefficient  $c_{p_a}$  related to the air pressure  $p_a$  is calculated as follows:

$$c_{p_a} = \frac{\partial F}{\partial p_a} = \frac{m}{\rho_b} \cdot [1 - \alpha_c(t_d - t_{d20})] \times \frac{\rho_b - \rho_w}{(\rho_w - \rho_a)^2} \times \frac{k_1}{t_a + t_{a0}} \quad (23)$$

$$c_{p_a} = \frac{\partial F}{\partial p_a} \approx \frac{m}{\rho_w^2} \cdot \frac{k_1}{t_a + t_{a0}} \quad (24)$$

If  $t_a = 20 \text{ }^\circ\text{C}$  is used:

$$c_{p_a} = \frac{\partial F}{\partial p_a} \approx 1,2 \times 10^{-9} \left( \frac{\text{kg}}{\text{m}^3} \text{K} \right)^{-1} \times m \quad (25)$$

The sensitivity coefficient  $c_\varphi$  related to the relative air humidity  $\varphi$  is calculated as follows:

$$c_\varphi = \frac{\partial F}{\partial \varphi} = \frac{m}{\rho_b} \times [1 - \alpha_c(t_d - t_{d20})] \times \frac{\rho_b - \rho_w}{(\rho_w - \rho_a)^2} \times \frac{k_2 t_a + k_3}{t_a + t_{a0}} \quad (26)$$

$$c_\varphi = \frac{\partial F}{\partial \varphi} \approx \frac{m}{\rho_w^2} \times \frac{k_2 t_a + k_3}{t_a + t_{a0}} \quad (27)$$

If  $t_a = 20 \text{ }^\circ\text{C}$  is used:

$$c_\varphi = \frac{\partial F}{\partial \varphi} \approx -1 \times 10^{-10} \left( \frac{\text{kg}}{\text{m}^3} \% \right)^{-1} \times m \quad (28)$$

The sensitivity coefficient  $c_{t_a}$  related to the air temperature  $t_a$  is calculated as follows:

$$c_{t_a} = \frac{\partial F}{\partial t_a} = \frac{m}{\rho_b} \cdot [1 - \alpha_c(t_d - t_{d20})] \times \frac{\rho_b - \rho_w}{(\rho_w - \rho_a)^2} \times \frac{\varphi k_2 t_{a0} - k_1 p_a - \varphi k_3}{(t_a + t_{a0})^2} \quad (29)$$

$$c_{t_a} = \frac{\partial F}{\partial t_a} \approx \frac{m}{\rho_w^2} \times \frac{\varphi(k_2 t_{a0} - k_3) - k_1 p_a}{(t_a + t_{a0})^2} \quad (30)$$

If  $\varphi = 50 \text{ } \%$ ,  $p_a = 1\,013 \text{ hPa}$ , and  $t_a = 20 \text{ }^\circ\text{C}$  are used:

$$c_{t_a} = \frac{\partial F}{\partial t_a} \approx -4,5 \times 10^{-9} \left( \frac{\text{kg}}{\text{m}^3} \text{K} \right)^{-1} \times m \quad (31)$$

## 5 Standard uncertainty associated with the volume delivered by a piston-operated volumetric apparatus

As mentioned in annex B of ISO 8655-6:—[2] there are two sources of uncertainty. One source is the uncertainty of the measurement of the delivered volume by the gravimetric method, the other is the uncertainty of the delivery process itself. By combining both, the standard uncertainty associated with the volume delivered by a piston-operated volumetric apparatus is obtained.

Equations (7) to (31) give the standard uncertainty associated with the volume  $V_{20}$  measured with the gravimetric measuring system. To derive the standard uncertainty associated with the volume delivered by a piston-operated volumetric apparatus (pipette, burette, etc.), the square of the experimental standard deviation (square of the random error of measurement, see 8.5 in ISO 8655-6:—[2]) of repeated measurements has to be treated as an additional term in equation (9). The sensitivity coefficient is 1 in this case ( $c_{V_{20}} = \frac{\partial V_{20}}{\partial V_{20}}$ ).

The standard uncertainty associated with the volume  $V_{20}$  measured with the gravimetric measuring system should be less than one third of the (expected) standard uncertainty associated with the volume delivered by the piston-operated volumetric apparatus which has to be calibrated. This ensures that the uncertainty obtained in the calibration is due mainly to the uncertainty caused by the piston-operated volumetric apparatus.

## 6 Standard uncertainties of measurement

It is possible to determine the standard uncertainties of measurement  $u(x)$  by making calibrations under repeatability conditions so as to obtain the experimental standard deviation associated with the repeatability (GUM: type A evaluation) or by considering the manufacturer's specifications of the measuring devices (e.g. for resolution, linearity, drift, temperature dependence).

In the second case, the manufacturer's specifications are often given as an interval covering the measurement value. The probability of finding the value within this interval is equal to 1. The distribution of possible values is uniform in this interval. This distribution is called rectangular (constant distribution inside the interval, zero distribution outside the interval). The interval should be used to give the variance in the form (GUM: type B evaluation) of:

$$u^2(x_i) = \frac{\left[ \frac{1}{2}(a_{i+} - a_{i-}) \right]^2}{3} = \frac{a_i^2}{3} \quad (32)$$

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

$a_i$  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.

## 7 Expanded uncertainty of measurement associated with volume $V_{20}$

The expanded uncertainty of the volume  $V_{20}$  is expressed as:

$$U = k \cdot u(V_{20}) \quad (33)$$

where the standard uncertainty is multiplied by the coverage factor  $k$ . The value  $k = 2$  is recommended for calibrations. In the case of a normal distribution, this means that when measuring the value of  $V_{20}$ , it can be found within the interval given by  $V_{20} \pm U$  ( $k = 2$ ) at a level of confidence of approximately 95 %.

The result of the measurement will therefore be given as:

$$V_{20} \pm U \quad (k = 2) \quad (34)$$

The coverage factor has to be stated.

## 8 Example for determining the uncertainty of the measurement

### 8.1 Measurement conditions

The measurement conditions are as follows:

- tenfold measurement of a nominal 100 µl volume of water, delivered by a piston-operated pipette;
- balance: 200 g balance with a readability of 10 µg;
- mean volume:  $V_{20} = 100,3 \mu\text{l}$ ;

- random error of measurement (experimental standard deviation):  $s(V_i) = 0,4 \mu\text{l}$ ;
- experimental standard deviation of the mean:  $s(V_{20}) = s(V_i)/\sqrt{n} = 0,13 \mu\text{l}$ ;
- systematic error of measurement:  $V_{20} - V_s = 0,3 \mu\text{l}$ .

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

**Table 1 — Determination of uncertainty**

Parameter		Interval	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient $c_i$	Uncertainty
		Equation (32)			Equations (11) to (31)	$c_i \times u(x_i)$
<b>Balance</b>	uncertainty	$\pm 100 \mu\text{g}$	rectangular	$57 \mu\text{g}$	$1 \text{ nl}/\mu\text{g}$	$57 \text{ nl}$
	linearity	$\pm 20 \mu\text{g}$	rectangular	$11,4 \mu\text{g}$	$1 \text{ nl}/\mu\text{g}$	$11,4 \text{ nl}$
	1 <sup>st</sup> value reproducibility	$\pm 20 \mu\text{g}$	rectangular	$11,4 \mu\text{g}$	$1 \text{ nl}/\mu\text{g}$	$11,4 \text{ nl}$
	2 <sup>nd</sup> value reproducibility	$\pm 20 \mu\text{g}$	rectangular	$11,4 \mu\text{g}$	$1 \text{ nl}/\mu\text{g}$	$11,4 \text{ nl}$
	1 <sup>st</sup> value readability	$10 \mu\text{g}$	rectangular	$2,9 \mu\text{g}$	$1 \text{ nl}/\mu\text{g}$	$2,9 \text{ nl}$
	2 <sup>nd</sup> value readability	$10 \mu\text{g}$	rectangular	$2,9 \mu\text{g}$	$1 \text{ nl}/\mu\text{g}$	$2,9 \text{ nl}$
	temperature drift	$0,1 \mu\text{g}$	rectangular	$0,029 \mu\text{g}$	$1 \text{ nl}/\mu\text{g}$	$0,029 \text{ nl}$
	correction for evaporation loss	$\pm 20 \mu\text{g}$	rectangular	$11,4 \mu\text{g}$	$1 \text{ nl}/\mu\text{g}$	$11,4 \text{ nl}$
<b>Water</b>	temperature	$\pm 0,1 \text{ K}$	rectangular	$5,7 \times 10^{-2} \text{ K}$	$20 \text{ nl}/\text{K}$	$1,14 \text{ nl}$
<b>Air</b>	temperature	$\pm 0,1 \text{ K}$	rectangular	$5,7 \times 10^{-2} \text{ K}$	$0,45 \text{ nl}/\text{K}$	$2,6 \times 10^{-2} \text{ nl}$
	pressure	$\pm 5 \text{ hPa}$	rectangular	$2,9 \text{ hPa}$	$0,12 \text{ nl}/\text{hPa}$	$0,35 \text{ nl}$
	relative humidity	$\pm 10 \%$	rectangular	$5,7 \%$	$0,01 \text{ nl}/\%$	$5,7 \times 10^{-2} \text{ nl}$
<b>Delivering device</b>	cubic expansion coefficient	$\pm 10^{-5} \text{ K}^{-1}$	rectangular	$5,7 \times 10^{-6} \text{ K}^{-1}$	$-2 \times 10^5 \text{ nl K}$	$1,14 \text{ nl}$
	temperature	$\pm 2 \text{ K}$	rectangular	$1,15 \text{ K}$	$1 \text{ nl}/\text{K}$	$1,15 \text{ nl}$
Standard uncertainty associated with the volume $V_{20}$ measured with the gravimetric measuring system						$61,6 \text{ nl}$
Experimental standard deviation of the mean of the calibration				$400/\sqrt{10} \text{ nl}$	1	$126 \text{ nl}$
Standard uncertainty of the calibration (for the mean delivered volume)				$(61,6^2 + 126^2)^{1/2} \text{ nl}$		$141 \text{ nl}$

## 8.2 Results

### 8.2.1 Standard uncertainty of the measurement

$$u(V_{20}) = 0,14 \mu\text{l}$$

### 8.2.2 Result of measurement

$$V_{20} = 100,30 \mu\text{l} \pm 0,28 \mu\text{l} (k=2)$$

### 8.2.3 Standard uncertainty of the calibration for one single delivered volume:

$$u(V_{20}) = (61,6^2 + 400^2)^{1/2} \text{ nl} = 405 \text{ nl} \approx 0,4 \text{ }\mu\text{l}.$$

Only a single dispensed volume is considered in this example. Therefore the experimental standard deviation is not divided by  $\sqrt{n}$  (see clause 5). This value has to be compared to values in the tables of maximum permissible random errors given in ISO 8655 (parts 2 to 5) [6], [7], [8], [9].

### 8.2.4 General remarks

It should be kept in mind that 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.

The uncertainty contributions of the balance reproducibility and the balance readability are listed twice as there are two readings giving the mass value before and after the delivery procedure.

The readability of the thermometer, the barometer, and the humidity measuring device are much smaller than the given intervals and are thus neglected.

The uncertainty associated with the gravimetric measurement is mainly attributed to the uncertainty associated with the result given by the balance.

The uncertainties attributed to the lack of knowledge of air temperature, pressure and humidity are often so small, that in most cases it is justifiable to work with standard values rather than the measured values.

For the same reason, it is often justifiable to neglect the uncertainty due to the thermal expansion of the piston-operated volumetric apparatus.

It should be kept in mind that, although the thermal expansion coefficient and the temperature of the piston-operated volumetric apparatus have been taken into consideration in this example, other factors have not been taken into consideration (e.g. the effect of an air interface of a piston-operated pipette which is non-saturated with water vapour).

For delivered volumes smaller than 100  $\mu\text{l}$ , it may be important to consider the error resulting from the evaporation of liquid. Nonetheless, the uncertainty due to evaporation has been calculated for this example (100  $\mu\text{l}$  volume measurement), as given in Table 1, and can be considered negligible.

The standard uncertainty associated with the volume  $V_{20}$  measured using the gravimetric measuring system is much smaller than the standard uncertainty associated with the calibration. This means the standard uncertainty is primarily attributed to the standard uncertainty of the volume delivered by the delivering device.

### 8.2.5 Note on the conformity of ISO 8655 with GUM

Random error of measurement is equivalent to the term "experimental standard deviation" used in GUM. There is no direct equivalent to systematic error of measurement in GUM. But a simple way to be in conformity with the GUM is to expand the model (paragraph 2) defining a new quantity  $V_d = V_{20} - V_s$ , where  $V_s$  is the selected volume of the piston-operated volumetric apparatus. In this case the result of the measurement is equivalent to the systematic error of measurement defined in ISO 8655-6. The measurement uncertainty will be unchanged as  $V_s$  has a zero uncertainty.

The systematic error of measurement does not influence the measurement uncertainty of the volume  $V_{20}$  measured with the gravimetric measuring system. It is the result of a measurement made using the gravimetric measuring system and has to be referred to the piston-operated volumetric apparatus. It is a measure characterizing the volume delivered by the piston-operated volumetric apparatus.

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1) To be published.

2) This review gives all constants based on the temperature scale ITS-90.



