

## ECOMET

ECOWAS COMMUNITY METROLOGY COMMITTEE


(GRAVIMETRIC METHOD]



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## ORIGINAL VERSION

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This document was produced with the financial support of the European Union.

[^0]This Document presents guidelines taken to calibrate volumetric instruments such as piston pipettes, hand dispensers (according to ISO 8655 / DKD-R 8-1), glassware adjusted as to deliver "Ex", such as Bulb pipettes (according to ISO 648), Graduated pipettes (according to ISO 835), Burettes for liquids (according to ISO 385), glassware adjusted as to contain "In", such as volumetric flasks (according to ISO 1042), graduated cylinders and mixing cylinders (according to ISO 4788), according to the requirements of ISO 4787.

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## 1 INTRODUCTION

Liquid volume measurement is an important step in most industrial and analytical measurement operations. Volume instruments are used in many fields like chemistry, health, biology, pharmacy industries, fuel depot, etc. In several applications within these fields, the measurement of volume is significant or critical, therefore it is important to ensure that volume quantities measured using these instruments are reliable. In order to identify and reduce possible errors in liquid handling, it is necessary to calibrate the volume instruments using the correct methods.

Volume instruments can be calibrated by filling, or emptying, using a reference volume measurement, i.e. by comparing two volumes (volumetric method). This is a secondary method of calibration. At the highest level of the traceability chain, the volume can be determined by the primary method of weighing the quantity of a suitable liquid, contained or delivered by the volume instrument, provided that the temperature and density of the liquid are known (gravimetric method).

It is also necessary to evaluate the measurement uncertainty as this information must accompany the final measurement result to give the end user confidence in the measurement.

## 2 REFERENCES

ISO 8655: Piston-Operation Volumetric Apparatus, 2002
ISO 4787: Laboratory glassware - Volumetric instruments - Methods for testing of capacity and for use, 2010
ISO 3696: Water for analytical laboratory use-specification and test method, 1987
OIMLR120: Calibration of standard capacity measures by gravimetric method, 2010

## 3 TERMINOLOGY AND SYMBOLS

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

## 4 APPARATUS

### 4.1 Weighing

Weighing is the most important step in gravimetric calibration. The weighing results are influenced by several factors such as the resolution and sensitivity of the balance, the calibration of the balance (eccentricity, linearity and repeatability), the class and density of the reference weights used to calibrate an electronic scale or balance. Balance with a resolution appropriate to the selected volume of the apparatus under test (see Table 1).

## Table 1

| Selected volume of apparatus under test | Resolution <br> $(\mathrm{mg})$ |
| :---: | :---: |
| $1 \mu \mathrm{l} \leq \mathrm{V} \leq 10 \mu \mathrm{l}$ | 0.001 |
| $10 \mu \mathrm{l}<\mathrm{V} \leq 100 \mu \mathrm{l}$ | 0.01 |
| $100 \mu \mathrm{l}<\mathrm{V} \leq 1000 \mu \mathrm{l}$ | 0.1 |
| $1 \mathrm{ml}<\mathrm{V} \leq 10 \mathrm{ml}$ |  |
| $10 \mathrm{ml}<\mathrm{V} \leq 200 \mathrm{ml}$ | 0.1 |
| 1 |  |

If the standard uncertainty of measurement of the balance is known (e.g. from the balance calibration certificate), this may be used instead of the repeatability and linearity. The standard uncertainty of measurement shall not be more than two to three times the resolution.

### 4.2 Liquid reservoir

With sufficient capacity for all the test liquid likely to be required for the complete series of tests.

### 4.3 Weighing vessel

Suitable for the test procedure selected. Care shall be taken regarding the loss of water by evaporation during the dispensing and weighing procedure. It is recommended that, especially for testing apparatus of the lowest volume, the height-to-diameter ratio of the weighing vessel be at least $3: 1$ or that a weighing vessel with a lid be used.

### 4.4 Volume instrument characteristics

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

## 5 AMBIENT CONDITIONS

The ambient conditions (air temperature, humidity, barometric pressure) influence gravimetric measurement mainly through the air density determination, so those quantities must be measured and recorded during the measurements because of the possible fluctuations. The calibration must be carried out after the temperature between the calibration object and the environment has been equalized. An equalization time of at least 2 hours must be observed for starting calibration.

## 6 METHOD

### 6.1 Gravimetric Method

The gravimetric method is the standard method used both by National Metrology Institutes (NMIs) and by accredited laboratories to calibrate volume instruments. The method consists of weighing the instrument under calibration when empty and again when full with appropriate liquid. The difference obtained in the weighing measurements gives the mass of contained or delivered liquid. Volume instruments are usually provided with reference marks in order to precisely define the volume being obtained. The volume adjustment with respect to those marks is very important for the measurement.
Also important are the draining and drying procedures of the volume instrument applied during calibration since they both affect the result. The liquid used is generally pure water (distilled or deionized) with a conductivity less than $5 \mu \mathrm{~S} / \mathrm{cm}$.

### 6.2 Volumetric Method

The method is applicable for the calibration of any size of volume measures for which standard pipets of comparable volume are available. Typical volume measures have volumes in the range of 100 mL to 20 L . The precision of calibration depends on the care exercised in adjusting the various volumes and strict adherence to the various steps of the procedure. The accuracy will depend on the accuracy of calibration of the volumetric standards used, accuracy in reading the meniscus, together with the precision of the comparison. Clean volume measure and strict adherence to the drainage instructions are essential for precise and accurate results.

### 6.2.1 Summary

The flask to be calibrated is given an initial wet-down using the correct drain procedure, then nearly filled with water delivered from a calibrated pipet. (This procedure relies on calibrated pipets that deliver slightly less than the full nominal volume.) Additional water is added to the test flask from a calibrated burette until the meniscus in the test item coincides with the calibration graduation mark. The sum of the volumes delivered into the wetted flask is equivalent to its "to deliver" volume. The process described assumes that the flask is marked with a 10 -second drain time. If the flask is marked with a drain time other than 10 s , the specified drain time should be used rather than the 10 s drain time described. A 30-second drain time should be used when a flask or can has no drain time specified.

### 6.3 Standards and Equipment

6.3.1 Calibrated standard volume measures of suitable volumes.
6.3.2 Calibrated standard burette(s) of 10 mL (or 120 minims) capacity. These standards are typically made of borosilicate glass. 11 [US] minim $=0.061615496$ millilitre ( mL ). 120 minim standards were provided to the ECOWAS Member States as reference standards for use in volume transfer calibrations. These standards have higher resolution than metric standards provided at the same time.
6.3.3 Calibrated thermometers, with resolution and uncertainty to $\leq 0.1^{\circ} \mathrm{C}$ to determine water temperature.
6.3.4 Meniscus reading device.
6.3.5 Stopwatch or other suitable timing device.

## 7 CALCULATION OF VOLUME AT $20^{\circ} \mathrm{C}$

The equation for the volume $V_{20}$ of the delivered water at $20^{\circ} \mathrm{C}$ is given by

$$
\begin{equation*}
V_{20}=m Z Y \tag{1}
\end{equation*}
$$

with

$$
\begin{equation*}
m=m_{F}-m_{E}-m_{\text {Evap }} \tag{2}
\end{equation*}
$$

where
$m \quad$ Mass of delivered water
$m_{E} \quad$ Balance reading of the empty weighing vessel
$m_{F} \quad$ Balance reading of the weighing vessel and the delivered water
$m_{\text {Evap }} \quad$ Balance reading of the mass loss due to evaporation of liquid during the measurement

Z Combined factor for buoyancy correction and conversion from mass to volume
$Y \quad$ Thermal expansion correction factor of the volumetric instrument

Equation (1) combines the measurement results yielded by the balance ( $m$ ), air and liquid densities yielded by measurements of air and liquid temperature, air pressure and relative humidity of air in conjunction with tables or equations for the factor $(Z)$, and parameters of the volumetric instrument $(Y)$
$Z$ is given by

$$
\begin{equation*}
Z=\frac{1}{\rho_{w}} \cdot \frac{1-\frac{\rho_{a}}{\rho_{b}}}{1-\frac{\rho_{a}}{\rho_{w}}}=\frac{1}{\rho_{a}} \cdot \frac{\rho_{b}-\rho_{a}}{\rho_{w}-\rho_{a}} \tag{3}
\end{equation*}
$$

where
$\rho_{w} \quad$ is the density of water
$\rho_{\mathrm{a}} \quad$ is the density of air
$\rho_{\mathrm{b}} \quad$ is the density of the standard weight used to calibrate the balance
[according to OIML (Organisation Internationale de Metrologie Legale), $\rho_{\mathrm{b}}=8000 \mathrm{~kg} / \mathrm{m}^{3}$ for steel weights]

The density of water $\rho_{\mathrm{w}}$ (in $\mathrm{kg} / \mathrm{m}^{3}$ ) can be calculated in the temperature range ( 5 to $40^{\circ} \mathrm{C}$ ) according to the following equation:

$$
\begin{equation*}
\rho_{w}=\sum_{i=0}^{4} a_{i} t_{w}^{i} \tag{4}
\end{equation*}
$$

where
$t_{w} \quad$ is the water temperature in ${ }^{\circ} \mathrm{C}$
with the constants (ITS-90 temperature scale):

$$
\begin{aligned}
& a_{0}=999.85308 \mathrm{~kg} / \mathrm{m}^{3} \\
& a_{1}=6.32693 \cdot 10^{-2}{ }^{\circ} \mathrm{C}^{-1} \mathrm{~kg} / \mathrm{m}^{3} \\
& a_{2}=-8.523829 \cdot 10^{-3}{ }^{\circ} \mathrm{C}^{-2} \mathrm{~kg} / \mathrm{m}^{3} \\
& a_{3}=6.943248 \cdot 10^{-5}{ }^{\circ} \mathrm{C}^{-3} \mathrm{~kg} / \mathrm{m}^{3} \\
& a_{4}=-3.821216 \cdot 10^{-7} \mathrm{o}^{-4} \mathrm{~kg} / \mathrm{m}^{3}
\end{aligned}
$$

The density of air $\rho_{a}$ (in $\mathrm{kg} / \mathrm{m}^{3}$ ) is given by

$$
\begin{equation*}
\rho_{a}=\frac{k_{1} p_{a}+\varphi\left(k_{2} t_{a}+k_{3}\right)}{t_{a}+t_{a 0}} \tag{5}
\end{equation*}
$$

where

$$
t_{a 0}=273.15^{\circ} \mathrm{C}
$$

$p_{\mathrm{a}}$ is the ambient pressure ( hPa )
$\varphi \quad$ is the relative humidity (\%)
$t_{a} \quad$ is the air temperature $\left({ }^{\circ} \mathrm{C}\right)$
with the constants (ITS - 90 temperature scale):

$$
\begin{aligned}
& k_{1}=0.34844\left(\mathrm{~kg} / \mathrm{m}^{3}\right)^{\circ} \mathrm{C} / \mathrm{hPa} \\
& k_{2}=-0.00252 \mathrm{~kg} / \mathrm{m}^{3} \\
& k_{3}=0.020582\left(\mathrm{~kg} / \mathrm{m}^{3}\right)^{\circ} \mathrm{C}
\end{aligned}
$$

The correction for the thermal expansion of the volumetric instrument is given by

$$
\begin{equation*}
Y=1-\alpha_{c}\left(t_{d}-t_{d 20}\right) \tag{6}
\end{equation*}
$$

where
$\alpha_{c}$ is the cubic expansion coefficient $\left({ }^{\circ} \mathrm{C}^{-1}\right)$
$t_{d}$ is the device temperature $\left({ }^{\circ} \mathrm{C}\right)$

$$
t_{d 20}=20^{\circ} \mathrm{C}
$$

Equations (1) to (6) can be expressed as:

$$
\begin{equation*}
V_{20}=\frac{m}{\rho_{b}} \cdot \frac{\rho_{b}}{\rho_{w}-} \frac{-\rho_{a}}{\rho_{a}} \cdot\left[1-a_{c}\left(t_{d}-t_{d 20}\right)\right] \tag{7}
\end{equation*}
$$

## 8 UNCERTAINTY OF MEASUREMENT

The model function 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.

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

$$
\begin{align*}
u^{2}\left(V_{20}\right) & =\left(\frac{\partial V_{20}}{\partial m}\right)^{2} u^{2}(m)+\left(\frac{\partial V_{20}}{\partial t_{w}}\right)^{2} u^{2}\left(t_{w}\right)+\left(\frac{\partial V_{20}}{\partial t_{a}}\right)^{2} \cdot u^{2}\left(t_{a}\right)+\left(\frac{\partial V_{20}}{\partial p_{a}}\right)^{2} u^{2}\left(p_{a}\right) \\
& +\left(\frac{\partial V_{20}}{\partial \alpha_{c}}\right)^{2} \cdot u^{2}\left(\alpha_{c}\right)+\left(\frac{\partial V_{20}}{\partial t_{d}}\right)^{2} u^{2}\left(t_{d}\right)+\left(\frac{\partial V_{20}}{\partial \varphi}\right)^{2} u^{2}(\varphi)+\left(\frac{\partial V_{20}}{\partial V_{20}}\right)^{2} \cdot u^{2}\left(s_{V_{20}}\right) \\
& +\left(\frac{\partial V_{20}}{\partial \rho_{w}}\right)^{2} \cdot u^{2}\left(\rho_{w}\right)+\left(\frac{\partial V_{20}}{\partial m_{\text {meniscus }}}\right)^{2} \cdot u^{2}\left(m_{\text {meniscus }}\right)+\left(\frac{\partial V_{20}}{\partial m_{\text {process_rel.handling }}}\right)^{2} \cdot u^{2}\left(m_{\text {process__rel.handling }}\right) \tag{8}
\end{align*}
$$

where:
$u^{2}\left(x_{i}\right)$ are the standard uncertainties referred to the measurement of each quantity which contributes to the final result (described by the model);
$c_{i}=\left(\frac{\partial V_{20}}{\partial x_{i}}\right)^{2}$ are the sensitivity coefficients giving the weight of each individual standard uncertainty.

The following sources of uncertainties contribute to the result of the measurement:

- Mass of delivered / contained water
- Water temperature / water density
- Air density
- Air temperature
- Air pressure
- Relative air humidity
- Temperature of volumetric instrument for glassware and standard measuring cans
- Thermal expansion coefficient for glassware and standard measuring cans
- Standard deviation or repeated measurements
- Meniscus reading only for glassware and standard measuring cans
- Process related handling influences only for piston pipettes
- Systematic influences due to the air cushion only for piston pipettes

The sensitivity coefficients may be determined by calculating the partial derivatives as indicated in equation (8).

As the uncertainties of the constants are very small compared to other uncertainties, they can be neglected in the evaluation of uncertainty.

### 8.1 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 $\rho_{w}-\rho_{a} \approx \rho_{w,} \rho_{b}-\rho_{a} \approx \rho_{b}, \rho_{w} \approx 1000 \mathrm{~kg} / \mathrm{m}^{3}$, $1-\alpha_{c}\left(t_{d}-t_{d 20}\right) \approx 1$ and $\rho_{b}-\rho_{w} \approx \rho_{b}$ are used without special notation.

The sensitivity coefficients in equation (8) are calculated as partial derivatives using equations (9) to (19).

The sensitivity coefficients $c_{m}$ related to the balance reading $m$ is calculated as follows:

$$
\begin{equation*}
c_{m}=\frac{\partial V_{20}}{\partial m}=\frac{V_{20}}{m} \approx \frac{1}{\rho_{w}}=10^{-3} \frac{\mathrm{~m}^{3}}{\mathrm{~kg}}=1 \frac{\mathrm{nl}}{\mu g} \tag{9}
\end{equation*}
$$

The sensitivity coefficient $\boldsymbol{C}_{\alpha c}$ related to the cubic expansion coefficient $\alpha_{c}$ of the volumetric instrument is calculated as follows:

$$
\begin{align*}
c_{\alpha_{c}}= & \frac{\partial V_{20}}{\partial \alpha_{c}}=-\frac{m}{\rho_{b}} \cdot \frac{\rho_{b}-\rho_{a}}{\rho_{w}-\rho_{a}} \cdot\left(t_{d}-t_{d 20}\right) \\
& \approx-\frac{m}{\rho_{w}} \cdot\left(t_{d}-t_{d 20}\right)=-10^{-3}\left(\frac{\mathrm{~kg}}{\mathrm{~m}^{3}}\right)^{-1} \cdot m \cdot\left(t_{d}-20^{0} C\right) \tag{10}
\end{align*}
$$

The sensitivity coefficient $c_{t d}$ related to the temperature $t_{d}$ of the volumetric instrument is calculated as follows:

$$
c_{t_{d}}=\frac{\partial V_{20}}{\partial t_{d}}=-\frac{m}{\rho_{b}} \cdot \frac{\rho_{b}-\rho_{a}}{\rho_{w}-\rho_{a}} \cdot \alpha_{c} \approx-\frac{m}{\rho_{w}} \cdot \alpha_{c}
$$

The sensitivity coefficient $c_{t w}$ related to the water temperature $t_{w}$ is calculated as follows:
$c_{t_{w}}=\frac{\partial V_{20}}{\partial t_{w}}=-\frac{m}{\rho_{b}} \cdot \frac{1-\alpha_{c}\left(t_{d}-t_{d 20}\right)}{\left(\rho_{w}-\rho_{a}\right)^{2}} \cdot\left(\rho_{b}-\rho_{a}\right) \cdot\left[\sum_{i=1}^{4} i a_{i} t_{w}^{i-1}\right]$
$c_{t_{w}}=-\frac{m}{\rho_{w}^{2}} \cdot \frac{\partial \rho_{w}}{\partial t_{w}}=-\frac{m}{\rho_{w}^{2}} \cdot\left[\sum_{i=1}^{4} i a_{i} t_{w}^{i-1}\right]$

It is possible to use the expression $\frac{\partial \rho_{w}}{\partial t_{w}}=-2.1 \cdot 10^{-4} \mathrm{~K}^{-1} \cdot \rho_{w}$ instead of the sum given in the equation (14) in the temperature range of $19{ }^{\circ} \mathrm{C}$ to $21^{\circ} \mathrm{C}$ with sufficient accuracy.

$$
\begin{equation*}
c_{t_{w}} \approx \frac{\mathrm{~m}}{\rho_{w}} \cdot 2.1 \cdot 10^{-4} K^{-1}=2.1 \cdot 10^{-7}\left(\frac{\mathrm{~kg}}{\mathrm{~m}^{3}} \mathrm{~K}\right)^{-1} \cdot m \tag{14}
\end{equation*}
$$

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


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

$$
\begin{equation*}
c_{\varphi}=\frac{\partial V_{20}}{\partial \varphi}=\frac{m}{\rho_{b}} \cdot\left[1-\alpha_{c}\left(t_{d}-t_{d 20}\right)\right] \cdot \frac{\rho_{b}-\rho_{w}}{\left(\rho_{w}-\rho_{a}\right)^{2}} \cdot \frac{k_{2} t_{a}+k_{3}}{t_{a}+t_{a 0}} \approx \frac{m}{\rho_{w}^{2}} \cdot \frac{k_{2} t_{a}+k_{3}}{t_{a}+t_{a 0}} \tag{16}
\end{equation*}
$$

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

$$
\begin{align*}
c_{t_{a}} & =\frac{\partial V_{20}}{\partial t_{a}}=\frac{m}{\rho_{b}} \cdot\left[1-\alpha_{c}\left(t_{d}-t_{d 20}\right)\right] \cdot \frac{\rho_{b}-\rho_{w}}{\left(\rho_{w}-\rho_{a}\right)^{2}} \cdot \frac{\varphi k_{2} t_{a 0}-k_{1} p_{a}-\varphi k_{3}}{\left(t_{a}+t_{a 0}\right)^{2}} \\
& \approx \frac{m}{\rho_{w}^{2}} \cdot \frac{\varphi\left(k_{2} t_{a 0}-k_{3}\right)-k_{1} p_{a}}{\left(t_{a}+t_{a 0}\right)^{2}} \tag{17}
\end{align*}
$$

The sensitivity coefficient $c_{s(V 20)}$ related to the standard deviation of repeated measurements is calculated as follows:

$$
\begin{equation*}
c_{s_{V 20}}=\frac{\partial V_{20}}{\partial V_{20}}=1 \tag{18}
\end{equation*}
$$

The sensitivity coefficient $\boldsymbol{C}_{\rho(w)}$ related to density of water is calculated as follows:

$$
\begin{equation*}
c_{\rho_{w}}=\frac{\partial V_{20}}{\partial \rho_{w}}=-\frac{m}{\rho_{w}^{2}} \tag{19}
\end{equation*}
$$

The sensitivity coefficient $c_{m \text { (meniscus) }}$ related to the meniscus (only for volumetric glassware and standard measuring cans) is calculated as follows:

$$
\begin{equation*}
c_{m_{\text {menisus }}}=\frac{\partial V_{20}}{\partial m_{\text {meniscus }}}=1 \tag{20}
\end{equation*}
$$

The sensitivity coefficient $c_{m \text { (roroc._reated handing) }}$ related to the process related handling contribution of the volumetric instrument (only for piston pipettes) is calculated as follows:

$$
\begin{equation*}
c_{m_{\text {proc_related handling }}}=\frac{\partial V_{20}}{\partial m_{\text {proc_related handling }}}=1 \tag{21}
\end{equation*}
$$

### 8.2 Standard Uncertainty associated with the Volume delivered / contained by a Volumetric Instrument

## Mass of delivered / contained water $m$ and $\delta m_{\text {evap: }}$ :

The balance reading is directly taken from the balance (empty vessel and filled vessel) and the uncertainty is taken from the calibration certificate of the balance (normal distribution with
$k=2$ or student distribution). The uncertainty is taken twice for empty vessel and filled vessel. The resolution of the balance is taken twice too (rectangular distribution).

The evaporation loss during measurement is determined experimentally. The correction for evaporation loss during measurement is taken to be zero. The value for the uncertainty is estimated for the different volumetric instruments as follows (rectangular distribution):

Table 2: Evaporation loss for different volumetric instruments (depending on nominal volume)

| Volume measures | Evaporation loss |
| :--- | :---: |
| Piston pipettes | $2 / 10 / 50 \mu \mathrm{~g}$ |
| Glassware to contain (In) | $100 / 500 \mu \mathrm{~g}$ |
| Glassware to deliver (Ex) | $100 \mu \mathrm{~g}$ |
| Standard measuring cans | $3000 \mu \mathrm{~g}$ |

## Water temperature / water density $t_{w} / \rho_{w}$ :

The water temperature is measured with a digital thermometer. The uncertainty is taken from the calibration certificate of the thermometer (normal distribution with $k=2$ ).

The maximum change during calibration is taken as $\pm 0.2 \mathrm{~K}$ (rectangular distribution).
The uncertainty for the equation used to calculate the density of water is estimated to be $\delta \rho_{w}$ $= \pm 10 \mathrm{ppm}$ (rectangular distribution).

## Air density $\rho_{a}$ :

## Air temperature $\boldsymbol{t}_{\mathrm{a}}$ :

The air temperature is measured with a Thermo-hydrometer. The uncertainty is taken from the calibration certificate of the Thermo-hydrometer (normal distribution with $k=2$ ). The maximum change during calibration is taken as $\pm 0.5 \mathrm{~K}$ (rectangular distribution).

## Air pressure $p_{\mathrm{a}}$ :

The air pressure is measured with a barometer. The uncertainty is taken from the calibration certificate of the barometer (normal distribution with $k=2$ ). The maximum change during calibration is taken as $\pm 1 \mathrm{hPa}$ (rectangular distribution).

## Relative air humidity $\varphi$ :

The relative air humidity is measured with a Thermo-hydrometer. The uncertainty is taken from the calibration certificate of the Thermo-hydrometer (normal distribution with $k=2$ ). The maximum change during calibration is taken as $\pm 5 \%$ (rectangular distribution).

## Temperature of volumetric instruments $\boldsymbol{t}_{\boldsymbol{d}}$ :

Temperature of the volumetric instruments is assumed to be the same as the water temperature. The uncertainty is taken from the calibration certificate of the digital thermometer (normal distribution with $k=2$ ). Due to different types and designs of the individual pipettes the cubic expansion coefficient cannot universally determined. For this reason, this contribution was not taken into account for piston pipettes.

## Thermal expansion coefficient $\alpha_{c}$ :

The thermal expansion coefficients for different materials are listed below. $10 \%$ of the thermal expansion coefficient is taken as standard uncertainty (rectangular distribution).

Table 3: Different materials and their thermal expansion coefficient for volumetric instruments

| Material | Thermal expansion coefficient $\alpha_{c}$ <br> in ${ }^{\circ} \mathrm{C}^{-1}$ |
| :--- | :---: |
| Brass / copper | $5.3 \cdot 10^{-5}$ |
| Stainless steel | $5.1 \cdot 10^{-5}$ |
| Aluminium | $6.9 \cdot 10^{-5}$ |
| Borosilicate glass | $9.9 \cdot 10^{-6}$ |
| Semi-borosilicate glass | $14.7 \cdot 10^{-6}$ |

Due to different types and designs of the individual pipettes, the cubic expansion coefficient cannot be universally determined. For this reason, this contribution was not taken into account for piston pipettes.

## Standard deviation or repeated measurements $s\left(V_{20}\right)$ :

The experimental standard deviation is calculated from the $n=10$ repeated measurements (normal distribution with $k=1$ ):

$$
\begin{equation*}
s\left(V_{20}\right)=\sqrt{\frac{\sum_{i=1}^{n}\left(V_{20 i}-\overline{V_{20}}\right)^{2}}{n-1}} \tag{22}
\end{equation*}
$$

## Meniscus $\boldsymbol{m}_{\text {meniscus: }}$

## Volumetric instruments with graduated scale:

The uncertainty due to the meniscus is estimated as the uncertainty in the volume determination due to the resolution $r$ of the scale. A triangular distribution is assumed and the standard uncertainty is estimated as:

$$
\begin{equation*}
u\left(m_{\text {meniscus }}\right)=\frac{r / 2}{\sqrt{6}} \tag{23}
\end{equation*}
$$

## Volumetric instruments with one-mark:

The uncertainty due to the meniscus is estimated as the uncertainty in the volume determination due to the positioning and determination of the meniscus' lowest point $u_{\rho}$ and the cross-section area $A$ of the volume measures where the air-water meniscus is located. A rectangular distribution is assumed and the standard uncertainty is estimated as:

$$
\begin{equation*}
u\left(m_{\text {meniscus }}\right)=\frac{u_{p} / 2 \cdot A}{\sqrt{3}}=\frac{u_{p} / 2 \cdot \frac{1}{4} \cdot \pi \cdot D^{2}}{\sqrt{3}} \tag{24}
\end{equation*}
$$

With $\quad u_{p}=0.5 \cdot d, d$ is width of scale mark, $A$ is cross section area and $D$ is diameter of volume measures where the air-water meniscus is located.

## Process-related handling contribution:

$u\left(m_{\text {process__rel. handing }}\right)=0.07 \%$ of volume for fixed volumes and $0.1 \%$ for variable volumes and multi-channel pipettes (rectangular).

## Systematic influences due to the air cushion:

- Temperature: difference between water, pipette and air $\pm 0.2 \mathrm{~K}$ (rectangular)
- Humidity: drift during calibration of $\pm 5 \%$ (rectangular);
- Atmospheric pressure: drift during calibration of $\pm 20 \mathrm{hPa}$ (triangular);

The sensitivity coefficients of these contributions are calculated empirically see DKDE 8-2.

### 8.3 Expanded Uncertainty of Measurement associated with Volume $\mathbf{V}_{20}$

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

$$
\begin{equation*}
U=k u\left(V_{20}\right) \tag{25}
\end{equation*}
$$

The standard uncertainty is multiplied by the coverage factor $k$. The coverage factor $k$ for an approximately $95 \%$ confidence level is 2 .

The result of the measurement which has to be stated in the calibration certificate is given as:

$$
\begin{equation*}
V_{20} \pm U(k=2) \tag{26}
\end{equation*}
$$

The coverage factor has to be stated in the calibration certificate.

## 9 <br> UNCERTAINTY BUDGET

| Quantity $\left(x_{i}\right)$ | Value | Distribution | Standard uncertainty $u\left(x_{i}\right)$ | Sensitivity coefficient $c_{i}$ | Uncertainty $u\left(y_{i}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Repeatability measurements ( $\mu \mathrm{L}$ ) | 0.135 |  | 0.135 | 1 | $1.35 \mathrm{E}-01$ |
| Weighing instrument (mg) | 1.1 | Normal | 0.1 | 1 | 1.00E-01 |
| Air Density (mg/ $\mu \mathrm{L}$ ) | 1.19 | rectangle | 0.577350269 | 0.00012 | 6.93E-05 |
| Water Density (mg/ $\mu \mathrm{L}$ ) | 998.14 | rectangle | $5.7735 \mathrm{E}-06$ | 100.37 | 5.80E-04 |
| Density of the mass pieces ( $\mathrm{mg} / \mu \mathrm{L}$ ) | 8000.00 | rectangle | 0 | 0 | 0.00E+00 |
| Coefficient of expansion from the micropipette material ( ${ }^{\circ} \mathbf{C}^{-1}$ ) | 0.00024 | rectangle | 6.9282E-06 | -0.03 | -2.08E-07 |
| Water temperature ( ${ }^{\circ} \mathrm{C}$ ) | 20.3 | Normal | 0.006 | 0.021 | $1.26 \mathrm{E}-04$ |
| Evaporation ( $\mu \mathrm{L}$ ) | 50 | rectangle | 0.028867513 | 1 | $2.89 \mathrm{E}-02$ |
| Other |  |  |  |  |  |
| Combined uncertainty ( $\mu \mathrm{L}$ ) |  |  |  |  | 0.170 |
| Coverage factor $k$ |  |  |  |  | 2 |
| Expanded uncertainty ( $\mu \mathrm{L}$ ) (k=2) |  |  |  |  | 0.340 |



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