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Calibration of single stroke dispensers and piston burettes

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Deutscher Kalibrierdienst (DKD) – German Calibration Service

Since its foundation in 1977, the German Calibration Service has brought together calibration laboratories of industrial enterprises, research institutes, technical authorities, inspection and testing institutes. On 3rd May 2011, the German Calibration Service was reestablished as a *technical body* of PTB and accredited laboratories.
This body is known as *Deutscher Kalibrierdienst* (DKD for short) and is under the direction of PTB. The guidelines and guides developed by DKD represent the state of the art in the respective areas of technical expertise and can be used by the *Deutsche Akkreditierungsstelle GmbH* (the German accreditation body – DAkkS) for the accreditation of calibration laboratories.
The accredited calibration laboratories are now accredited and supervised by DAkkS as legal successor to the DKD. They carry out calibrations of measuring instruments and measuring standards for the measurands and measuring ranges defined during accreditation. The calibration certificates issued by these laboratories prove the traceability to national standards as required by the family of standards DIN EN ISO 9000 and DIN EN ISO/IEC 17025.

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Foreword

DKD guidelines are application documents that meet the requirements of DIN EN ISO/IEC 17025. The guidelines contain a description of technical, process-related and organizational procedures used by accredited calibration laboratories as a model for defining internal processes and regulations. DKD guidelines may become an essential component of the quality management manuals of calibration laboratories. The implementation of the guidelines promotes equal treatment of the equipment to be calibrated in the various calibration laboratories and improves the continuity and verifiability of the work of the calibration laboratories. By implementing the guidelines, it is possible to incorporate the current level of development in the respective fields into laboratory practice.

The DKD guidelines should not impede the further development of calibration procedures and processes. Deviations from guidelines as well as new procedures are permitted in agreement with the accreditation body if there are technical reasons to support this action.

Calibrations by accredited laboratories provide the user with the security of reliable measuring results, increase the confidence of customers, enhance competitiveness in the national and international markets, and serve as metrological basis for the monitoring of measuring and test equipment within the framework of quality assurance measures.

The present guideline has been drawn up by DKD's Technical Committee *Chemical Measurands and Material Properties* / Subcommittee *Volume and Density* in cooperation with PTB and accredited calibration laboratories and has been approved by the Board of the DKD. The Guidelines DKD-R 8-1 "Calibration of piston-operated pipettes with air cushion", DKD-R 8-2 "Calibration of Multiple Delivery Dispensers" and DKD-R 8-3 "Calibration of single stroke dispensers and piston burettes" form a series of publications dealing with the calibration of piston-operated volume measuring devices.

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1. Purpose and scope of application

This guideline defines the minimum requirements for the calibration procedure, taking into account special influences and measurement uncertainty contributions in the calibration of single-stroke dispensers and piston burettes, with and without motor drive.
For devices with exchange dosing units, the definitions and requirements refer to the combination of basic device and dosing unit used.

Applicable standards and regulations

DIN EN ISO 8655 Part 1, 3, 5, 6	Volumenmessgeräte mit Hubkolben (English title: Piston-operated volumetric apparatus)
ISO/TR 20461	Determination of uncertainty for volume measurements made using the gravimetric method, November 2000 / Technical Corrigendum 1, December 2008
JCGM 100: 2008	Evaluation of measurement data – Guide to the expression of uncertainty in measurement, September 2008
EURAMET cg-18 (Calibration Guide No. 18)	Guidelines on the Calibration of Non-Automatic Weighing Instruments, Version 4.0 (11/2015), https://www.euramet.org/publications-media-centre/calibration-guidelines/
DKD-R 7-2	Richtlinie zur Kalibrierung nichtselbsttätiger Waagen, Ausgabe 01/2018 (German translation of the EURAMET Calibration Guide No. 18 Version 4.0), https://doi.org/10.7795/550.20180928
EURAMET cg-19 (Calibration Guide No. 19)	Guidelines on the Determination of Uncertainty in Gravimetric Volume Calibration, Version 3.0 (09/2018), https://www.euramet.org/publications-media-centre/calibration-guidelines/
DIN ISO 3696	Wasser für analytische Zwecke, Anforderungen und Prüfungen, June 1991 (English title: Water for analytical laboratory use, specification and test methods)
EA-4/02 M: 2013	Ermittlung der Messunsicherheit bei Kalibrierungen (German translation), release of the first edition: 18 October 2013, translation: 01.08.2019, DAkkS, https://www.dakks.de/doc_kalibrier (English title: Evaluation of the uncertainty of measurement in calibration)

2. Symbols

2.1 Abbreviations and symbols

Abbreviations / symbols	Explanation
c	Sensitivity coefficient
m	Mass of the test liquid corresponding to the difference of the scale readings
m_{E}	Evaporation loss
n	Number of individual measurements
p_{L}	Air pressure
s	Random measurement error
t_{W}	Temperature of the test liquid in °C
t_{L}	Air temperature during weighing in °C
t_{M}	Temperature of the single stroke dispenser / the piston burette during measurement in °C
t_{M20}	Reference temperature of the single stroke dispenser / piston burette of 20 °C
u	Standard measurement uncertainty
U	Expanded measurement uncertainty (k = 2)
V_0	Nominal volume
V_{S}	Selected volume
V_{20}	Volume at a reference temperature of 20 °C according to the gravimetric method
$V_{20,\mathrm{ges.}}$	Volume at a reference temperature of 20 °C, taking into account all input / influencing variables
ρ_{L}	Air density
ρ_{W}	Density of the water used as test liquid
ρ_{G}	Density of the standard weights used to calibrate the balance (equivalent to 8000 kg/m^3)
ϕ	Relative humidity
γ	Cubic expansion coefficient of the overall system

2.2 Units

Units	Explanation
µl	Microlitres
ml	Millilitres
g	Gram
mg	Milligram
K	Kelvin
°C	Centigrade
hPa	Hectopascal
g/cm^3	Grams per cubic centimetre
µl/mg	Microlitres per milligram

3. Terms and definitions

Calibration certificate:
Calibration certificates are used to document the results of calibrations, including their measurement uncertainty. Within this guideline, the term “calibration certificate” is limited to the following documents:

- calibration certificates of calibration laboratories whose accreditation bodies are signatories of ILAC-MRA (see https://ilac.org/)
- calibration certificates of National Metrology Institutes with CMC entries (Appendix C, CIPM MRA, see https://www.bipm.org).

For information purposes, the following terms, definitions and descriptions from **DIN EN ISO 8655-1** are listed below:

Dispensers:
Dispensers are used for the repeated dispensing (dosing) of measured volumes of liquid. Single stroke dispensers deliver a single dosage per filling stroke. Multiple dispensers or devices with stepwise resolution deliver several doses per filling stroke.

Piston burettes:
Piston burettes are used for continuous dosing of liquid until reaching a volume that meets external (usually analytical) criteria, such as colour change, pH, conductivity or polarisation. The dosed volume can be read on a display or otherwise recorded by the instrument (see ISO 8655-3).

Useful volume:
The useful (also called effective) volume of a volume measuring device with variable volume constitutes a sub-range of the nominal volume within which dosing can be carried out in compliance with the error limits specified in the international standard ISO 8655. The upper limit of the effective volume is defined by the manufacturer.

Selected volume:
The selected volume V_S of a volume measuring device with variable volume is the volume set by the user to dose a selected volume from the effective volume of a piston stroke device. In case of volume measuring devices with fixed volume, the selected volume corresponds to the nominal volume.

Nominal volume:
The nominal volume V_0 of a volume measuring device is the volume defined by the manufacturer for identification and specification of the measuring range.
The nominal volume is usually reached with a full stroke of the dosing unit, but not with continuously operating piston burettes.

4. Aim of the calibration

The calibration of single stroke dispensers and piston burettes is used to determine the deviation of the dosed volume from the selected test volume. The metrological accuracy – including the consideration of the measurement uncertainty of the determined measurement results – is decisive for implementing quality-relevant metrological specifications/requirements in medicine, pharmacy, etc. The metrological traceability to national or international standards has to be ensured.

Note: According to DIN EN ISO/IEC 17025:2018 (ISO/IEC 17025:2017), the comparability of calibration results must be ensured by national and international interlaboratory comparisons / comparison measurements. The basis for conducting such comparisons is laid down in DIN EN ISO/IEC 17043:2010.

5. General requirements for the calibration capability of single stroke dispensers and piston burettes

The general requirements regarding the calibration capability of single stroke dispensers and piston burettes can be divided into three categories:

- requirements according to DIN EN ISO 8655
- requirements from the manufacturers' product information
- additional requirements from common practice

5.1 Requirements from DIN EN ISO 8655

For calibrations, the requirements of Part 1, Part 3, Part 5 and Part 6 of EN ISO 8655 are to be implemented, insofar as this guideline does not restrict or specify the requirements.

5.2 Requirements from the manufacturers’ product information

These requirements vary depending on the specification and scope of the product information provided by the respective manufacturer. Among the most important requirements are:

- information regarding operation, exclusions of use, care and cleaning
- indication of type and manufacturer of the dosing unit
- indication of the manufacturer's specification, including the permissible tolerances of the random and systematic measurement error with respect to adjustment (In/Ex) and reference temperature

5.3 Requirements resulting from observation during calibration

The requirements resulting from everyday practice mainly concern the immediate operational capability of the single stroke dispensers and piston burettes. These include among others:

- Marking of the volume measuring devices by indicating
    - serial number, or another unique identification number
    - manufacturer and type
    - nominal volume

- Indication of the accessories used. The manufacturer's instructions must be followed.

- Avoidance of internal and external damage to the
    - housing
    - discharge tube (dispensing cannula)
    - filling (suction) tube
    - recirculation valve
    - control elements
    - drive unit, if applicable

- If necessary, checking the state of charge of the accumulator or battery
- Leak test of the system according to the manufacturer's specifications

6. Ambient conditions

To obtain precise measurement results, the calibration has to be carried out under stable ambient conditions.

The ambient conditions

- air temperature
- relative humidity
- air pressure

affect the

- weighing technology
- calibration item
- test liquid

and, therefore, have a significant influence on the calibration result of the calibration item and the associated uncertainty budget.

Compliance with specified ambient conditions by means of air conditioning is an important prerequisite for calibration. The calibration is to be carried out after temperature equalisation between the calibration item and the environment. An adequate stabilisation time of the calibration item of at least 2 h close to the calibration location is to be observed. For calibration items of a larger mass, it might be necessary to select a longer stabilisation time. The ambient conditions at the time of calibration are to be recorded.

It must also be ensured that fluctuations in the ambient conditions are observed and recorded during calibration.

7. Calibration procedure

The calibration of the calibration items is carried out according to the gravimetric procedure as described in DIN EN ISO 8655-6 in which the mass of the liquid's volume is determined from the weight value, taking into account the air buoyancy, and converted into volume by means of the liquid density. The volume is metrologically traced back to the measurand of mass. A complete calibration includes the measurement (metrological recording) of 10 measured values per test volume.

Preferably, the measuring devices used are analytical balances with evaporation traps. Minimum requirements for the weighing instruments to be used are defined in ISO 8655-6.

7.1 Calibration items

Single stroke dispensers and piston burettes are volumetric instruments which are directly connected to a reservoir (usually a flask) of the test liquid via a suction tube or suction hose.
Note: For motor burettes, the bottle is located next to the dosing unit.

In case of single stroke dispensers, the test liquid is drawn up to the beginning of the stroke and dispensed into a dosing vessel in a single step. Single stroke dispensers are often also referred to as bottle top dispensers.
With piston burettes, liquid is dispensed into a dosing vessel up to the selected volume. The setting is carried out manually, by handwheels, or by means of a motor.

7.2 Additional information for calibration (supplementary to DIN EN ISO 8655-6)

The following instructions/information apply for preparation and calibration.

Piston burettes

Preparing for calibration:

- The measuring instrument, weighing vessel and storage vessel with test liquid must be adapted to the ambient conditions in the vicinity of the balance (at least 2 h or, for devices of a larger mass, a longer stabilisation time)

- Weighing vessel:
  A narrow neck vessel with standard ground joint is recommended.
  - Prepare some test liquid.
  - Weighing vessel is swivelled to saturate the atmosphere.
  - Wait briefly to create the required climate in the narrow neck vessel (e.g. Erlenmeyer flask).

- Assembling the piston burette:
  - If necessary, select a suitable adapter for the storage vessel.
  - Connect filling tube to the piston burette, paying attention to length. Establish hose connections for motor burettes according to operating instructions. The filling tube must not be sealed by standing on the bottom of the storage vessel.
  - Connect the piston burette – corresponding to type and design – to the storage vessel according to the operating instructions (when using motor burettes, please pay attention to special features).
  - The manufacturer’s instructions must be observed when connecting the output cannula.

- Removing air from the piston burette (priming):
  - Turn the handwheels up and down quickly several times until no more air bubbles can be seen on the piston and in the output cannula.
  - In case of motor burettes, priming according to operating instructions.

Calibration:

- If applicable, raise the piston to the stop.
- Dispense a few drops to compensate for play and wipe them off at the weighing vessel (or a similar vessel) while holding the burette at an angle. These drops do not form part of the dosed volume.
  With motor burettes, the compensation for play is usually carried out automatically.
- Place the weighing vessel under the output cannula with the cannula reaching a few millimetres into the weighing vessel.
- Tare the weighing vessel.
- The test liquid is dispensed in a free jet.
  In case of motor burettes, the output cannula should be held in the upper part of the weighing vessel to prevent splashing.
- Set the display to zero before starting the calibration.
- Operate the handwheels evenly and with both hands at moderate speed to dispense the test liquid up to the desired volume; in case of motor-driven burettes the discharge (dispensing) is motorised.
- At the end of the discharge, turn the handwheels more slowly to precisely adjust the volume (the display must not be overtightened).
- For motor burettes reduce discharge speed if necessary.
- Droplets at the end of the cannula belong to the dosed volume and are wiped off at an angle on the weighing vessel.
- Only the precisely dosed, selected volume is to be used. Otherwise the measurement is to be repeated.

Single stroke dispenser

Preparation:

- Measuring instrument, weighing vessel and storage vessel containing the test liquid must be adapted to the ambient conditions close to the weighing instrument (at least 2 h or, in the case of instruments with a larger mass, a longer stabilisation time).
- Weighing vessel:
  - A narrow neck vessel with standard ground joint is recommended; some test liquid should be kept at hand.
  - The weighing vessel is to be moved to saturate the atmosphere.

  - In order to create the necessary climate in the narrow neck vessel, a short waiting time is to be observed, see above

- Assembling the single stroke dispenser:
  - Select a suitable adapter for the storage vessel.
  - Connect filling tube to the single stroke dispenser, paying attention to length. The filling tube must not be sealed by standing on the bottom of the storage vessel.
    Connect the single stroke dispenser – corresponding to type and design – to the storage vessel according to the operating instructions.
    The filling tube must not be sealed by standing on the bottom of the storage vessel.
  - Establish hose connections for motor dispensers according to the operating instructions.
  - The manufacturer's instructions must be observed when connecting the output cannula.

- Removing air from the single stroke dispenser (priming):
  - The piston in the lower area should be moved quickly up and down, several times and with short strokes, until no more air bubbles can be seen on the piston and in the discharge cannula.
  - In case of motor dispensers, air is to be removed according to operating instructions.

Calibration:

- Pull the piston upwards until it stops, making sure that the piston is pulled **straight** upwards; in case of motor-driven devices, the piston can be moved to the starting position by motor force; if necessary, compensate for play.
- **Gently approach the upper stop.**
- Wipe off droplets at the end of the cannula on the weighing vessel (or similar vessel) at an angle to obtain an identical meniscus before and after dosing (**does not belong to the dosed volume**).
- Tare the weighing vessel.
- Hold the weighing vessel at a slight angle against the cannula and discharge the test liquid by pressing down the piston.

- **Gently approach the lower stop.**
- Wipe off droplets at the end of the cannula, holding it at an angle (**does not belong to the dosed volume**).

8. Measurement uncertainty

The measurement uncertainty is a parameter that is stated along with the measurement result. The measurement uncertainty is determined by the measurement procedure and is assigned to the measurement result. The measurement uncertainty characterises a range of values that can reasonably be attributed to the measurand by means of measurement.

As a matter of principle, the calculation of the uncertainty is performed according to the international guide JCGM 100 “Evaluation of measurement data - Guide to the expression of uncertainty in measurement”, or in accordance with EA-4/02 M: 2013.

The uncertainty should be expressed as relative uncertainty as a percentage.

ISO/TR 20461, for the determination of the measurement uncertainty by means of the gravimetric method, is taken into account when drawing up the uncertainty budget. According to ISO/TR 20461, the volume for a reference temperature of 20 °C is calculated as follows:

$$V_{20} = \frac{m}{\rho_{\mathrm{G}}} \cdot \frac{\rho_{\mathrm{G}} - \rho_{\mathrm{L}}}{\rho_{\mathrm{W}} - \rho_{\mathrm{L}}} \cdot \left[1 - \gamma (t_{\mathrm{M}} - t_{\mathrm{M20}})\right] \quad (1)$$

Moreover, the formulae for calculating water density and air density must be taken into account. The following equation is used to calculate the standard uncertainty:

$$u^2(V_{20}) = \left(\frac{\partial V_{20}}{\partial m}\right)^2 \cdot u^2(m) + \left(\frac{\partial V_{20}}{\partial t_{\mathrm{w}}}\right)^2 \cdot u^2(t_{\mathrm{w}}) + \left(\frac{\partial V_{20}}{\partial \rho_{\mathrm{w}}}\right)^2 \cdot u^2(\rho_{\mathrm{w}}) + \left(\frac{\partial V_{20}}{\partial t_{\mathrm{L}}}\right)^2 \cdot u^2(t_{\mathrm{L}}) + \left(\frac{\partial V_{20}}{\partial p_{\mathrm{L}}}\right)^2 \cdot u^2(p_{\mathrm{L}}) + \left(\frac{\partial V_{20}}{\partial \phi}\right)^2 \cdot u^2(\phi) \quad (2)$$

In accordance with OIML-R 111, the uncertainty of the material density of the weights is negligible in relation to the resulting volume.
The influences of the temperature dependence of the material of the calibration item are dealt with in section 8.6.

The calculation of the sensitivity coefficients in equation (2) is shown in ISO/TR 20461.

In addition to the contributions of the gravimetric method, the following influencing variables are considered:

- system-related influences
- repeatability
- process-related handling contribution

With regard to these influencing variables, equation (2) must be extended in accordance with the uncertainty propagation law.

$$u^2(V_{20,\mathrm{ges.}}) = \left(\frac{\partial V_{20}}{\partial m}\right)^2 \cdot u^2(m) + \left(\frac{\partial V_{20}}{\partial t_\mathrm{w}}\right)^2 \cdot u^2(t_\mathrm{w}) + \left(\frac{\partial V_{20}}{\partial \rho_\mathrm{w}}\right)^2 \cdot u^2(\rho_\mathrm{w}) + \left(\frac{\partial V_{20}}{\partial t_\mathrm{L}}\right)^2 \cdot u^2(t_\mathrm{L}) + \left(\frac{\partial V_{20}}{\partial p_\mathrm{L}}\right)^2 \cdot u^2(p_\mathrm{L}) + \left(\frac{\partial V_{20}}{\partial \phi}\right)^2 \cdot u^2(\phi) + c_{\mathrm{syst.infl.}}^2 \cdot u^2(V_{\mathrm{syst.infl.}}) + c_{V_{20}}^2 \cdot u^2(V_\mathrm{s}) + c_{V_{20}}^2 \cdot u^2(V_{\mathrm{Handling}}) \quad (3)$$

A sensitivity coefficient of 1 is applied for the additional influencing variables.

The following cause-and-effect diagram provides a comprehensive presentation of all input/ influence quantities on the measurement uncertainty considered by this guideline.

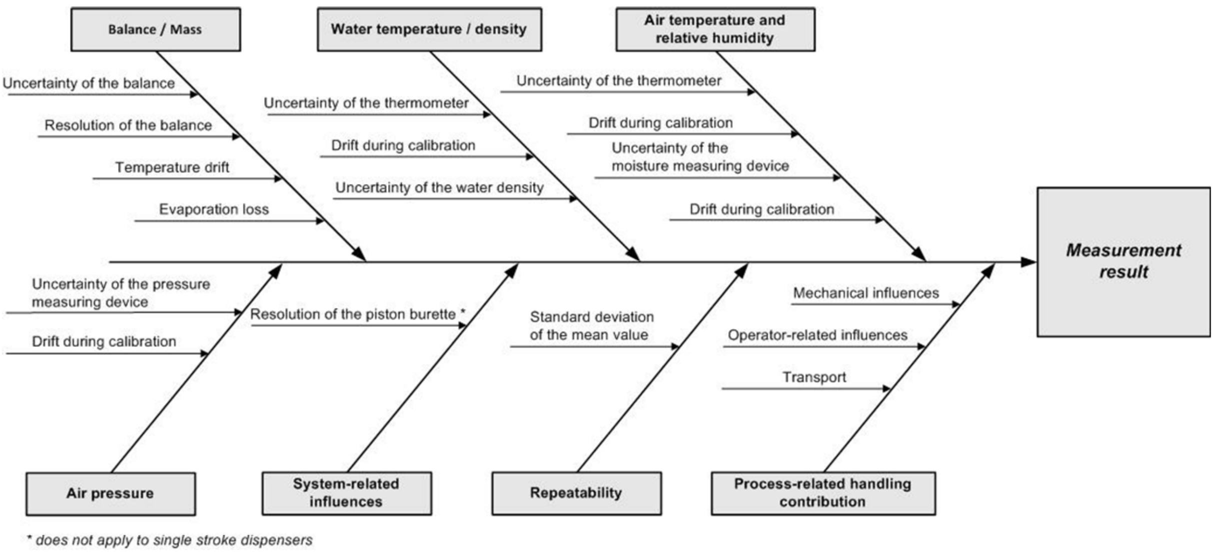

Figure 1: Illustration of the influences to be considered when determining the expected value and measurement uncertainty in the calibration of single stroke dispensers and piston burettes

8.1 General information

The accredited uncertainty budgets for the measurands and the calibration procedures constitute the prerequisite for ensuring national and international comparability of measurement results.

The uncertainty budgets for gravimetric calibration procedures comprise the following:

- improvement and determination of the calibration procedure,
- definition of specific ambient conditions,
- metrological evaluation of different calibration items from different instrument manufacturers,
- consideration of the process-related handling contribution.

The process-related handling contribution depends on the design and the operator. This uncertainty contribution is composed of random and systematic components.

In case that individual influences on the calibration result and its measurement uncertainty cannot be exactly determined, their contribution to the uncertainty is to be estimated and taken into account. The basis/source for this estimation is to be stated.

The measurement conditions of the calibration are to be described as completely as possible, given that the measurement uncertainties also depend on the conditions of use.

For comparative measurements, the calibration conditions should be defined (fixed) to ensure the comparability of the measurement results.

The uncertainties described below serve as a basis for the determination of the smallest assignable measurement uncertainties (“best measurement capability”) which are reflected in the accreditation. These uncertainties are part of the calibration and measurement capabilities (CMC).
The concept of the CMC is defined in EA-4/02 M: 2013.

8.2 Uncertainty contributions of the weighing instrument

Basically, it is assumed that the ambient conditions are nearly identical for the calibration of the balance and for the gravimetric calibration of the dispensers.

The calibration task, the measuring range and the resolution of the balance as well as the associated uncertainty are to be adjusted to each other to ensure the user-specific application according to EURAMET cg-18. The recommendations of ISO 8655 Part 6 are to be observed. The balance should be calibrated for the specific user, i.e. the measuring range of the calibration task should correspond to the calibrated weighing range.

The calibration of the balance according to EURAMET cg-18 must be ensured prior to the gravimetric calibration of the dispensers. Thus, the contributions attributed to the weighing, such as the resolution of the balance, the repeatability, the off-centre load (if no balance with an evaporation trap is used) and the display deviation are included in the current calibration certificate of the balance.

The calibration certificate of the balance used is the basis for further uncertainty considerations of the gravimetric procedure. The uncertainty contribution of the reading or resolution of the balance is included twice in the uncertainty budget (tare and gross weighing). The result of the weighing is the difference of the weight values.

Since the calibration is carried out according to the gravimetric method, regular observation of the balance is of great importance. This requires intermediate tests to be performed within the calibration period, using suitable calibrated weights.

An additional contribution results from the drift of the balance caused by aging and wear. This influence can be determined by intermediate testing or recalibration. After long-term surveillance, the contribution can thus be taken into account, and conclusions may be drawn. In the uncertainty budgets shown, this contribution has not been considered.

As a further contribution, the influence of the ambient temperature according to the manufacturer’s specifications is to be taken into account. This contribution can be taken from the manufacturer’s specification.

During the dosing process with the calibration items, open liquid surfaces occur. Therefore, an evaporation loss should be considered as a contribution.
The evaporation loss can be determined, or it can be estimated based on personal experience in relation to the volume of the calibration item.

8.3 Uncertainty contributions “water temperature / water density”

Before and during calibration, it must be ensured that the water used is free of bubbles and adjusted to the air temperature (deviation of ≤ 0,5 K). Otherwise, the measurement uncertainty must be adjusted accordingly.

Compliance with the specified ambient conditions “air temperature / relative humidity” during calibration is ensured by means of appropriate air conditioning. Hence, also the stability of the water temperature is positively influenced.

The temperature of the test liquid used (water) is determined by means of a calibrated thermometer. The uncertainty of the thermometer and the fluctuation of the water temperature (< 0,2 K) during calibration are taken into account in the uncertainty budget.

The influence of the temperature in the weighing vessel may be neglected.

The uncertainty for the calculation of the water density according to [1] is estimated at $10 \cdot 10^{-6}$ since neither the exact isotope ratio nor the gas content are known. The water density is required to calculate the volume of the test liquid.

8.4 Uncertainty contributions "air temperature and relative humidity"

During calibration, the ambient conditions "air temperature and relative humidity" are realised in predetermined parameters by means of air conditioning. The measurement data of the ambient conditions are recorded and documented using suitable, calibrated thermometers and humidity sensors.

The air density can be calculated according to equation (4) of EURAMET cg-19.

The air temperature variation during calibration should be ≤ 0,5 K.

The relative humidity should be ≥ 45 %. Low air humidity favours static charging of the weighing instruments.

Note: The calibration of single stroke dispensers and piston burettes with smallest assignable measurement uncertainties within the scope of the CMC requires the ambient conditions to be maintained within small tolerance limits.

8.5 Uncertainty contribution "air pressure"

The air pressure should be recorded and documented using a calibrated precision barometer. The air pressure is a necessary measurement quantity for calculating the air density and thus the volume. The precision barometer used should have a resolution of 1 hPa or better.

8.6 System-related influences

The thermal expansion of single stroke dispensers and piston burettes is made up of the expansion of the cross section of the dosing unit and the expansion of the distance between the stroke stops or the expansion of the stroke measuring system.
The expansion of the cross section of the dosing unit is usually small, given that the material used is mostly glass. However, there are also dosing units made of plastic which show a higher expansion.

By removing the air before calibration, it can be assumed that the temperature of the dosing units has adapted itself, to a large extent, to the temperature of the test liquid.
The expansion of the dosing unit and the water show a negative correlation, i.e. they reduce each other. These are the two influences described in equation (17) and equation (20) of ISO/TR 20461.
If the expansion of the cross section of the dosing unit is not included in the uncertainty budget, then this represents a maximum estimation of the influence of the test liquid's temperature. The inclusion of the thermal expansion of the dosing unit's cross section into the budget may therefore be omitted.

In the case of single stroke dispensers and piston burettes, hand heat is usually not expected to be introduced. Therefore, there is no corresponding contribution to the budget.

If the volume is to be related to a reference temperature differing from the measuring temperature (temperature of the test liquid) – as expressed in equation (6) in ISO/TR 20461 – it is necessary to know the thermal expansion coefficient of the entire system of the stroke mechanism or stroke measuring system and the cross-section of the dosing unit, including the uncertainty of this coefficient.
In this case, the resulting uncertainty according to equation (15) in ISO/TR 20461 must be considered in the uncertainty budget. As there are usually no data for the thermal expansion of the overall system – by contrast to volume measuring instruments made of glass – it is recommended to state the water temperature as reference temperature. Thus, this contribution can be omitted.

The resolution of the piston burette is considered in the uncertainty budget as a system-dependent influence and equals one display digit. To determine the uncertainty contribution, half the value of the resolution is assigned to the half width of the rectangular distribution.

8.7 Repeatability

The repeatability is understood to be the empirical standard deviation of the mean value of a series of 10 individual measurements. The empirical standard deviation characterises the dispersion of the measured values under the same measuring conditions during the calibration of the mentioned volume measuring devices; it is calculated according to the following formula:

$$s = \sqrt{\frac{\sum_{i=1}^{n} (V_\mathrm{i} - \bar{V})^2}{n-1}} \qquad (4)$$

The standard uncertainty (confidence interval of the mean value) of the repeatability is determined according to method A (GUM) and is calculated using the following formula:

$$u(s) = \frac{s}{\sqrt{n}} \qquad (5)$$

Experience has shown that the experimental standard deviation is about one third of the tolerance specified by the manufacturer for the repeatability (maximum random measurement deviation).
A normal distribution can be assumed.

8.8 Handling / device

When calculating the uncertainty for a certain type of device, the design of the device must be taken into account as the components of the uncertainty (device and handling surcharge) depend on this design. It is recommended to use the manufacturer's tolerances for accuracy when calculating the handling contribution.

An uncertainty contribution of 1/6 of the manufacturer's tolerance for accuracy is used as best approximation and consideration of all influences for handling. This contribution represents a minimum value which may not fall below.
A rectangular distribution can be assumed.

Based on the statistical evaluation of selected manufacturer's tolerances, the following values are recommended for establishing the uncertainty budget.
These are relative values which refer to the nominal volume.

Process-related handling surcharge for dispensers

up to	1 ml nominal volume	0.15 %
from	1 ml nominal volume	0.08 %

Process-related handling contribution for piston burettes

above	25 ml	0.01 %
up to	25 ml	0.012 %
up to	10 ml	0.02 %

These are minimum values. If indicated by experience and manufacturer's tolerances, it may be necessary to increase these values.

8.9 Uncertainty budgets

Note: Two uncertainty budgets are attached to this document.

Annex A Single stroke dispenser 10 ml

Annex B Piston burette 25 ml

DKD-R 8-3 provides the basis for calibration practice in accredited calibration laboratories when calibrating single stroke dispensers and piston burettes. It describes fundamental influences on the measurement uncertainty. Thus, the comparability between the calibration laboratories is ensured, giving the possibility for national and international comparison measurements. The aim is to incorporate the results of the guideline activities of the Technical Subcommittee of the DKD into the ongoing development of the work and activities on DIN EN ISO 8655.
In order to illustrate the various individual contributions, these are shown and individually calculated in the following uncertainty budgets. Thus, the order of magnitude of the individual contributions to the measurement uncertainty is easier to determine.

9. Bibliography

[1] M. TANAKA, G. GIRARD, R. DAVIS, A. PEUTO, N. BIGNELL: Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports; Metrologia 2001, 38, 301-309

Annex A Single stroke dispenser 10 ml

Quantity X_i	Best estimate x_i	Half width of the distribution a	Probability distribution $P(x_i)$	Divisor k	Standard uncertainty $u(x_i)$	Sensitivity coefficient $\|c_i\|$	Uncertainty contribution $u_i(y)$
Balance / Mass *m*							
Uncertainty of the balance	995.80 mg	191 µg	normal	2	95.500 µg	0.001 µl/µg	0.096 µl
Resolution of the balance (with load)	0 mg	50 µg	rectangular	$\sqrt{3}$	28.868 µg	0.001 µl/µg	0.029 µl
Resolution of the balance (without load)	0 mg	50 µg	rectangular	$\sqrt{3}$	28.868 µg	0.001 µl/µg	0.029 µl
Temperature drift	0 mg	0.5 K	rectangular	$\sqrt{3}$	0.289 K	0.001 µl/K	0.0003 µl
Evaporation loss	0 mg	100 µg	rectangular	$\sqrt{3}$	57.735 µg	0.001 µl/µg	0.058 µl
Water temperature t_W							
Uncertainty thermometer	20.8 °C	0.012 K	normal	2	0.006 K	2.1 µl/K	0.013 µl
Drift during calibration	0 °C	0.2 K	rectangular	$\sqrt{3}$	0.115 K	2.1 µl/K	0.242 µl
Water density ρ_W	998.03 kg/m³	10 ppm	rectangular	$\sqrt{3}$	0.0000058 mg/µl	10000 µl²/mg	0.058 µl
Air temperature + t_L							
Uncertainty thermometer	21.0 °C	0.13 K	normal	2	0.065 K	0.045 µl/K	0.0029 µl
Drift during calibration	0 °C	0.5 K	rectangular	$\sqrt{3}$	0.289 K	0.045 µl/K	0.013 µl
Air pressure p_L							
Uncertainty barometer	996.0 hPa	0.05 hPa	normal	2	0.025 hPa	0.012 µl/hPa	0.00030 µl
Drift during calibration	0 hPa	1 hPa	rectangular	$\sqrt{3}$	0.577 hPa	0.012 µl/hPa	0.0069 µl
Humidity + ϕ							
Uncertainty humidity sensor	49 %	0.6 %	normal	2	0.300 %	0.0010 µl/%	0.00030 µl
Drift during calibration	0 %	5 %	rectangular	$\sqrt{3}$	2.887 %	0.0010 µl/%	0.0029 µl
Repeatability $u(V_s)$	0 µl	3.33 µl	normal	$\sqrt{10}$	1.054 µl	1	1.054 µl
Process-related handling contribution $u(V_{Handling})$	0 µl	8.33 µl	rectangular	$\sqrt{3}$	4.811 µl	1	4.811 µl
$V_{20,ges.}$ (Volume)	9991.7 µl					***$u(V_{20,ges.})$* =**	4.93 µl
						***$U(V_{20,ges.})$* =**	**9.9 µl**
						***$w(V_{20,ges.})$* =**	0.049 %
						***$W(V_{20,ges.})$* =**	0.099 **%**

+ *the air buoyancy in the balance / evaporation trap is decisive*

Annex B Piston burette 25 ml

Qunatity X_i	Best estimate x_i	Half width of the distribution a	Probability distribution $P(x_i)$	Divisor k	Standard uncertainty $u(x_i)$	Sensitivity coefficient $\lvert c_i \rvert$	Uncertainty contribution $u_i(y)$
Balance / Mass *m*							
Uncertainty of the balance	24904.07 mg	212 µg	normal	2	106.000 µg	0.001 µl/µg	0.106 µl
Resolution of the balance (with load)	0 mg	50 µg	rectangular	$\sqrt{3}$	28.868 µg	0.001 µl/µg	0.029 µl
Resolution of the balance (without load)	0 mg	50 µg	rectangular	$\sqrt{3}$	28.868 µg	0.001 µl/µg	0.029 µl
Temperature drift	0 mg	0.5 K	rectangular	$\sqrt{3}$	0.289 K	0.025 µl/K	0.007 µl
Evaporation loss	0 mg	100 µg	rectangular	$\sqrt{3}$	57.735 µg	0.001 µl/µg	0.058 µl
Water temperature t_W							
Uncertainty thermometer	20.8 °C	0.012 K	normal	2	0.006 K	5.25 µl/K	0.032 µl
Drift during calibration	0 °C	0.2 K	rectangular	$\sqrt{3}$	0.115 K	5.25 µl/K	0.606 µl
Water density ρ_w	998.03 kg/m³	10 ppm	rectangular	$\sqrt{3}$	0.0000058 mg/µl	25000 µl²/mg	0.144 µl
Air temperature + t_L							
Uncertainty thermometer	21.0 °C	0.13 K	normal	2	0.065 K	0.113 µl/K	0.007 µl
Drift during calibration	0 °C	0.5 K	rectangular	$\sqrt{3}$	0.289 K	0.113 µl/K	0.032 µl
Air pressure p_L							
Uncertainty barometer	996.0 hPa	0.05 hPa	normal	2	0.025 hPa	0.03 µl/hPa	7.5E-04 µl
Drift during calibration	0 hPa	1 hPa	rectangular	$\sqrt{3}$	0.577 hPa	0.03 µl/hPa	0.017 µl
Humidity + ϕ							
Uncertainty humidity sensor	49 %	0.6 r.F.	normal	2	0.300 %	0.0025 µl/%	7.5E-04 µl
Drift during calibration	0 %	5 %	rectangular	$\sqrt{3}$	2.887 %	0.0025 µl/%	0.007 µl
Resolution piston burette $u(V_{syst.infl.})$	0 µl	5 µl	rectangular	$\sqrt{3}$	2.887 µl	1	2.89 µl
Repeatability $u(V_s)$	0 µl	2.1 µl	normal	$\sqrt{10}$	0.659 µl	1	0.659 µl
Process-related handling contribution $u(V_{Handling})$	0 µl	2.9 µl	rectangular	$\sqrt{3}$	1.684 µl	1	1.684 µl
$V_{20,ges.}$ **(Volume)**	24988.76 µl						

$u(V_{20,ges.})$ =	3.47 µl
$U(V_{20,ges.})$ =	**7.0 µl**
$w(V_{20,ges.})$ =	0.014 %
$W(V_{20,ges.})$ =	**0.028 %**

+ *the air buoyancy in the balance / evaporation trap is decisive*

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