INTERNATIONAL STANDARD

ISO 8655-6

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Piston-operated volumetric apparatus —

Part 6: **Gravimetric methods for the determination of measurement error**

Appareils volumétriques à piston —

Partie 6: Méthodes gravimétriques pour la détermination de l'erreur de mesure

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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.

Attention is drawn to the possibility that some of the elements of this part of ISO 8655 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 8655-6 was prepared by Technical Committee ISO/TC 48, *Laboratory glassware and related apparatus*, Subcommittee SC 1, *Volumetric instruments*.

ISO 8655 consists of the following parts, under the general title *Piston-operated volumetric apparatus*:

— *Part 1: Terminology, general requirements and user recommendations*

— *Part 2: Piston pipettes*

— *Part 3: Piston burettes*

— *Part 4: Dilutors*

— *Part 5: Dispensers*

— *Part 6: Gravimetric methods for the determination of measurement error*

The following part is under preparation:

— *Part 7: Non-gravimetric methods for the determination of measurement error*

Annex A forms a normative part of this part of ISO 8655. Annex B is for information only.

Introduction

ISO 8655 addresses the needs of:

— suppliers, as a basis for quality control including, where appropriate, the issuance of supplier's declarations;

— test houses and other bodies, as a basis for independent certification;

— users of the equipment, to enable routine checking of accuracy.

The tests specified should be carried out by trained personnel.

Piston-operated volumetric apparatus —

Part 6:
Gravimetric methods for the determination of measurement error

1 Scope

This part of ISO 8655 specifies the reference method for conformity testing of piston-operated volumetric apparatus, whereby errors of measurement are determined gravimetrically. The tests are applicable to complete systems comprising the basic apparatus and all parts selected for use with the apparatus, disposable or reusable, involved in the measurement by uptake (In) or delivery (Ex) process.

NOTE General requirements and definitions of terms of piston-operated volumetric apparatus are given in ISO 8655-1. For the metrological requirements, maximum permissible errors, requirements for marking and information to be provided for users for piston-operated volumetric apparatus, see ISO 8655-2 for piston pipettes, see ISO 8655-3 for piston burettes, see ISO 8655-4 for dilutors and see ISO 8655-5 for dispensers. Alternative test methods such as photometric and titrimetric methods will be the subject of a future Part 7 to ISO 8655.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 8655. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 8655 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 8655-1:2002, *Piston-operated volumetric apparatus — Part 1: Terminology, general requirements and user recommendations*

ISO 8655-2:2002, *Piston-operated volumetric apparatus — Part 2: Piston pipettes*

ISO 8655-3:2002, *Piston-operated volumetric apparatus — Part 3: Piston burettes*

ISO 8655-4:2002, *Piston-operated volumetric apparatus — Part 4: Dilutors*

ISO 8655-5:2002, *Piston-operated volumetric apparatus — Part 5: Dispensers*

ISO/TR 20461:2000, *Determination of uncertainty for volume measurements made using the gravimetric method*

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

OIML R 76-1:1992, *Non-automatic weighing instruments — Part 1: Metrological and technical requirements — Tests*

3 Terms and definitions

For the purposes of this part of ISO 8655, the terms and definitions given in ISO 8655-1, ISO/IEC Guide 2 and OIML R 76-1 apply.

4 Apparatus

4.1 Analytical balance or equivalent weighing device, with a resolution appropriate to the selected volume of the apparatus under test (see Table 1).

Table 1 — Minimum requirements for balances

Selected volume[a] of apparatus under test V	Resolution mg	Repeatability and linearity mg	Standard uncertainty of measurement mg
1 µl $\leqslant V \leqslant$ 10 µl	0,001	0,002	0,002
10 µl $< V \leqslant$ 100 µl	0,01	0,02	0,02
100 µl $< V \leqslant$ 1 000 µl	0,1	0,2	0,2
1 ml $< V \leqslant$ 10 ml	0,1	0,2	0,2
10 ml $< V \leqslant$ 200 ml	1	2	2

[a] For practical purposes, the nominal volume may be used to choose the balance.

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 from clause 7. 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 Timing device, with a standard uncertainty of $\leqslant$ 1 s (see note to 4.7).

4.5 Thermometer, with a standard uncertainty of $\leqslant$ 0,2 °C (see note to 4.7).

4.6 Hygrometer, with a standard uncertainty of $\leqslant$ 10 % (see note to 4.7).

4.7 Barometer, with a standard uncertainty of $\leqslant$ 0,5 kPa (see note to 4.7).

NOTE All uncertainties are specified using a coverage factor k of 1.

5 Test liquid

Use distilled or deionized water conforming grade 3 as specified in ISO 3696, degassed or air-equilibrated. The water shall be at room temperature (see 6.2).

6 Test conditions

6.1 General

Apparatus that is routinely dismantled and reassembled within the scope of its intended use (e.g. for cleaning purposes) shall be dismantled and reassembled at least once prior to the test in accordance with the supplier's operation manual.

Apparatus shall be operated as specified in the supplier's operation manual.

6.2 Test room

The test shall be carried out in a draught-free room with a stable environment. The test room shall have a relative humidity above 50 % and a constant (± 0,5 °C) temperature between 15 °C and 30 °C. Prior to the test, the apparatus to be tested and the test water shall have stood in the room for a sufficient time, at least 2 h, to reach equilibrium with the room conditions.

NOTE See 8.3 for corrections to be made when the balance readings are converted to volumes.

6.3 Evaporation

Especially for small volumes below 50 µl, errors due to evaporation of the test liquid during weighing shall be taken into consideration. Apart from the design of the weighing vessel (4.3), the test cycle time is important.

In order to keep the error due to evaporation as small as possible, the following additional items can be considered, if volumes below 50 µl are tested:

— a balance with appropriate accessories such as an evaporation trap could be used; or

— the test liquid to be weighed could be delivered into a capillary tube, although this method does not replicate the normal method of use and the user should verify for himself that correlation exists.

Regardless of these items, the error due to evaporation during the measuring series can be determined experimentally (see 7.2.8) and compensated mathematically (see 8.1). The uncertainty of this compensation should be added to the uncertainty of measurement.

6.4 Test cycle time

The test cycle time (time required to complete the weighing of one dispensed volume) shall be kept to a minimum. It should ideally not exceed 60 s. It is important that it is regular, both within each cycle and as far as possible from cycle to cycle, so that a reliable mathematical compensation of the error due to evaporation during the measuring series can be applied.

7 Procedure

7.1 General

7.1.1 Test volume

In the case of a fixed-volume apparatus, the test volume is the nominal volume. In the case of a variable-volume (user-selectable volume) apparatus, at least three volumes shall be tested:

— the nominal volume,

— approximately 50 % of the nominal volume,

— the lower limit of the useful volume range or 10 % of the nominal volume (whichever is the greater).

Measurement of further volumes is optional. The setting devices of the apparatus (e.g. dials, scales) shall be sufficient for the selection of the test volume.

7.1.2 Number of measurements per test volume

If the gravimetric methods of this part of ISO 8655 are used as conformity tests or type tests, e.g. prior to a declaration or certification of conformity, or if the gravimetric method is used as a reference method, 10 measurements for each test volume shall be carried out. These measurements are used to calculate the systematic and the random error of measurement in accordance with clause 8.

For re-establishing conformity, e.g. after repairs not performed by the supplier, 10 measurements at each volume shall also be performed.

If the gravimetric method is used for other purposes, such as supplier's quality control or supplier's after-sales service,

— the number of test volumes (see 7.1.1),

— the number of measurements per volume and,

— where applicable, the number of channels tested

may be changed to an appropriate number. Alternative test methods may also be used for this purpose, provided that they can be proven to correlate with the reference method specified in this part of ISO 8655, in which case the user should choose a number of measurements for his metrological confirmation based on his accuracy requirements.

7.1.3 Weighing procedure

Weighing for apparatus designed to deliver (Ex) shall always involve dispensing of the test liquid into the weighing vessel. Weighing for apparatus designed to contain (In) shall always involve the removal of test liquid from the weighing vessel. An example of the latter is the sample uptake step in the use of a dilutor.

7.1.4 Test conditions during the weighing procedure

At the start and at the end of the weighing procedure, the temperature of the test liquid in its container shall be recorded to the nearest 0,2 °C. The barometric pressure in the test room shall be recorded to the nearest 1 kPa and the relative humidity to the nearest 10 %.

7.2 Single-channel piston pipettes with air interface (in accordance with ISO 8655-2)

7.2.1 In the case of power-driven piston pipettes, aspiration and delivery of test liquid are automatic. The remainder of the procedure is carried out following the procedure described below.

7.2.2 Place test liquid from the water container in the weighing vessel to a depth of at least 3 mm. Record the temperature of the test liquid and the barometric pressure and relative humidity in the test room (see 7.1.4). If the weighing vessel has a lid, fit it.

NOTE Temperature and barometric pressure are necessary for the choice of the correction factor Z (see 8.3 and annex A); the relative humidity is not necessary for the evaluation as the correction factors Z in annex A apply to relative humidities ranging from 20 % to 90 % but are necessary for documentation in the test report [see clause 9, item d)].

7.2.3 If using a variable-volume piston pipette, select the test volume; this setting shall not be altered during the test cycle of 10 measurements.

7.2.4 Prepare the piston pipette and the test cycle as follows:

a) Fit the selected tip to the piston pipette.

b) Fill the tip with test liquid and expel to waste five times to reach a humidity equilibrium in the dead air volume (see ISO 8655-1:2002, 3.1.8) of the air-displacement piston pipette.

c) Place the weighing vessel with its added water on the balance pan.

7.2.5 Perform the following test cycle (see Figure 1 and Figure 2):

a) Replace the disposable tip of the piston pipette.

b) Fill the piston pipette with test liquid, immersing its delivery orifice 2 mm to 3 mm below the surface of the water. Release the operating button slowly, if hand operated, and withdraw the pipette vertically and carefully from the surface of the water. Touch the delivery orifice against the side wall of the container with the test liquid.

c) Expel the water to waste in order to pre-wet the tip and refill the piston pipette as described in b).

d) Record the mass m_0 of the weighing vessel to the nearest readable graduation as in Table 1, or tare the balance to zero ($m_0 = 0$). Start the timing device (this may be omitted if using a weighing vessel with lid).

e) If the weighing vessel has a lid, remove it. Deliver the contents of the pipette into the weighing vessel, touching the delivery end of the pipette tip against the inside wall of the vessel just above the liquid surface at an angle of approximately 30° to 45° and draw it approximately 8 mm to 10 mm along the inner wall of the weighing vessel to remove any droplets at or around the tip orifice. Replace the lid if applicable.

Where applicable, use the blow-out feature of the piston pipette to expel the last drop of liquid before drawing the delivery end of the tip along the inner wall of the weighing vessel.

If it is necessary to remove the weighing vessel from the balance pan to permit delivery of the dispensed volume, avoid excessive handling and possible contamination by the use of lint-free gloves. Return the weighing vessel to the balance pan after delivery.

f) Record the mass m_1 of the weighing vessel, or if tared in step 7.2.4 c) the mass m_i of the quantity delivered.

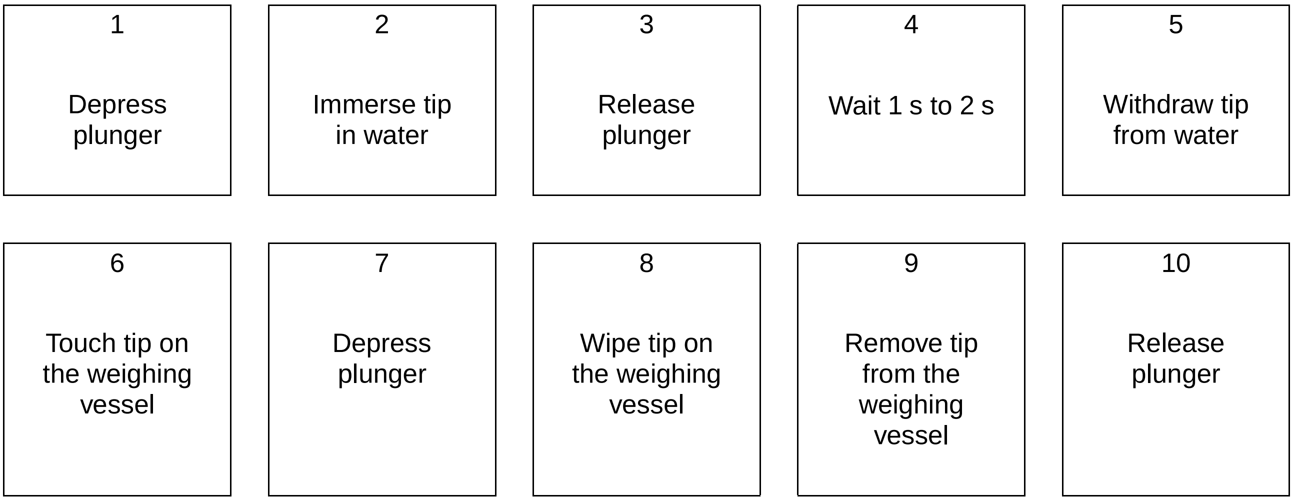

Figure 1 — Pipetting of testing volume into the weighing vessel

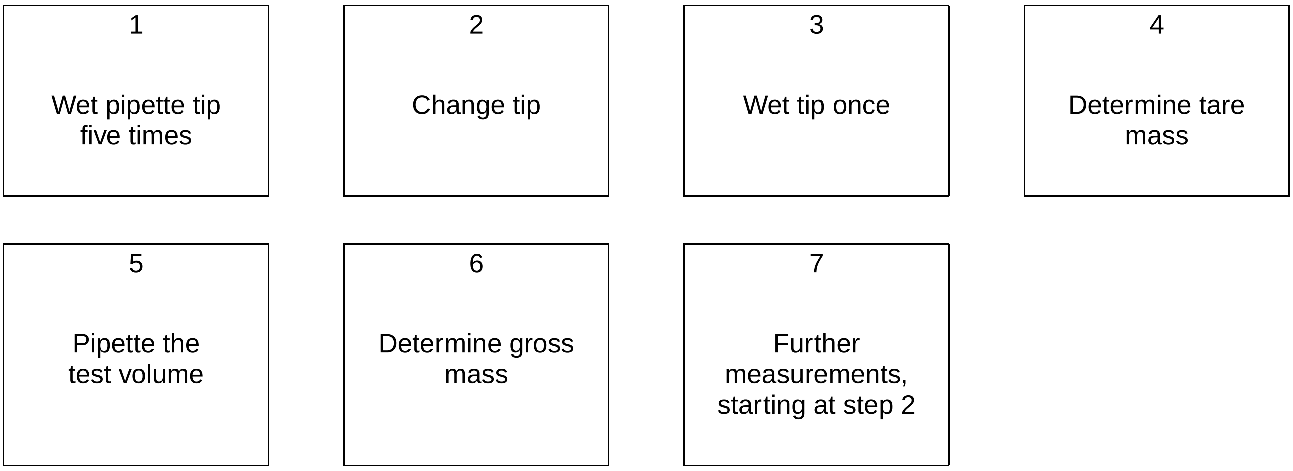

Figure 2 — Scheme of test procedure for piston pipettes with air interface

7.2.6 Repeat the test cycle described in 7.2.5 until 10 measurements have been recorded as a series of masses m_1 to m_{10}.

7.2.7 Note the time to the nearest second taken to complete the 10 test cycles.

7.2.8 After the last weighing of 7.2.6 leave the weighing vessel on the balance pan for the time measured in 7.2.7 and record its mass m_{11}.

If the weighing vessel was removed from the balance pan to enable delivery, leave it on the pan for half the time in 7.2.7 and then remove it from the balance and allow it to stand on the workbench for half the time measured in 7.2.7.

If the test volume is > 50 µl or if a weighing vessel with lid is used, omit steps 7.2.7 and 7.2.8, as a correction for evaporation is unnecessary. At 50 µl and below, calculate the mass loss in accordance with the supplier's instructions.

7.2.9 Measure the temperature of the remaining test liquid to the nearest 0,2 °C and calculate and record the mean test temperature (see 7.1.4).

7.2.10 The values obtained shall be evaluated in accordance with clause 8.

7.3 Multi-channel piston pipettes (in accordance with ISO 8655-2)

Multi-channel piston pipettes are similar to single-channel in that they comprise a set of single-volume measuring and delivery units all operated simultaneously by a single operating mechanism. For the purposes of the test, each channel shall be regarded as a single channel and tested and reported as such.

Fill all channels of the multi-channel pipette by aspirating the test liquid. Expel only the test liquid aspirated by the channel being tested into the weighing vessel.

7.4 Positive-displacement pipettes (in accordance with ISO 8655-2)

Piston pipettes without an air interface shall be tested in accordance with 7.2. However, the five-fold prewetting of the pipette tip prior to the test and the single prewetting before each measurement only need be performed if required by the supplier. Only change the pipette tips when testing positive-displacement pipettes of type D2 (see ISO 8655-2). Wipe the pipette tip on the water container wall after aspiration of the test liquid and prior to expelling it into the weighing vessel in order to remove droplets from the outside of the tip. Without removing liquid from the inside of the pipette tip, further remove any droplets that may still be present after the wiping of the tip. Follow the supplier's instructions regarding air-bubble-free filling of the pipette tip.

Empty the contents of the pipette tip into the weighing vessel as specified in 7.2.5 e).

7.5 Piston burettes (in accordance with ISO 8655-3)

7.5.1 Preparation

Carry out the testing by delivery into the weighing vessel (see 7.1.3). Carefully clean the weighing vessel and add a small quantity of test liquid to it. Place the weighing vessel and its test liquid in the balance case. Then place the burette under test, with its reservoir already filled with test liquid, as close to the balance as possible. Leave both for at least 2 h to come to equilibrium.

7.5.2 Test procedure

Measure the mass of the weighing vessel and its test liquid and consider this value as the tare mass prior to the first measurement.

Load the piston burette, bubble free, with test liquid from the reservoir, in accordance with the supplier's instructions. Deliver the test liquid from the burette into the weighing vessel, until the selected volume is reached. If the burette is automatically controlled, deliver test liquid until the volume preset is reached and no further delivery occurs. Weigh the weighing vessel again and calculate the mass of liquid delivered.

When testing partial volumes (see 7.1.1) of the nominal volume of the piston burette, the piston need not be reset to the initial position (zero) prior to the next measurement. Ensure that the upper volume limit of the piston and thus the nominal volume of the piston burette is not exceeded when dispensing a partial volume.

When testing piston burettes — especially in the case of automated tests — wiping of the delivery jet on the vessel wall to remove droplets can be impossible due to the individual test setup. In such cases, ascertain that the weighing is carried out only after a complete drop has been delivered from the delivery jet into the weighing vessel.

The test liquid can, for example, be expelled through an extended tip in such a way that the stream breaks and no drops form.

The values obtained shall be evaluated in accordance with clause 8.

7.6 Dilutors (in accordance with ISO 8655-4)

7.6.1 General

Depending on the design of the dilutor to be tested, sample volume, diluent volume and/or total volume shall be tested by performing 10 measurements. If sample volume (In) or diluent volume (Ex) is to be tested independently, the cylinder not being tested shall be set to zero or switched off, if the design permits. If it does not, only sample volume and total volume can be tested by usual operation.

7.6.2 Preparation

Carefully clean the weighing vessel (see 4.3) and add a small quantity of test liquid. If the sample uptake is to be measured, the volume of liquid shall be at least 15 times the volume to be aspirated at each operation. Consider the mass of the vessel including the test liquid prior to the first measurement as the tare mass [see also 7.2.4 c)]. Place the weighing vessel and its test liquid in the balance case. Then place the dilutor, with its diluent system properly filled and air-bubble-free, as close to the balance as practicable and leave it for at least 2 h to equilibrate.

If testing sample uptake, set the dilutor sample volume to the desired volume for the test, which may be the maximum or an intermediate volume within the range, and switch off the diluent system, set it to zero or set it to the minimum as available. Do not change these settings for the duration of the series of 10 measurements.

If testing diluent or total delivery, switch off the sample uptake system, set it to zero or set it to any convenient volume as available. Set the diluent volume to either the nominal volume or an intermediate volume within the range. Do not change these settings for the duration of the series of 10 measurements.

When testing dilutors with test volume settings of less than 50 µl, pay special attention to the evaporation of the test liquid from the weighing vessel as this may lead to substantial errors in measurement of delivered (or residual, in the case of withdrawal by aspiration of test liquid) mass. Balances as shown in Table 1 equipped with special accessories (e.g. evaporation traps) may be used.

7.6.3 Test procedure

Before carrying out the test, perform one complete cycle of aspiration and delivery (if necessary including delivery of test liquid from the diluent system) and discharge the test liquid to waste, in order to standardize the starting conditions. Touch the uptake and delivery probe against the side of the weighing vessel to remove droplets from around its orifice and weigh the weighing vessel to establish its starting mass.

Measure the sample volume by aspirating the test liquid from the weighing vessel via the aspiration and delivery probe, and record the mass lost from the weighing vessel. Touch the end of the probe against the inside wall of the weighing vessel after aspiration to ensure that no random droplets adhere round its orifice. Discharge the aspirated sample to waste, if necessary with a quantity of “diluent” test liquid. Measure the diluent volume using the diluent delivery system as a dispenser, if possible. Otherwise, measure the total of the sample volume together with the diluent volume.

NOTE Many designs of dilutor permit use as dispensers by inactivation of the sample aspiration facility.

If the total volume is measured by aspiration of test water from the weighing vessel and then expulsion with “diluent” test liquid back into the weighing vessel, the increase in mass will be accounted for only by “diluent” test liquid. In either case, the increase in mass of the weighing vessel corresponds to a single delivery of “diluent” test liquid.

During operation, ensure that the piston does not hit the stroke limits too quickly which could provoke a brief opening of the spring-loaded exhaust valve (spitting caused by the recoil force of the abruptly interrupted flow).

The values obtained shall be evaluated in accordance with clause 8.

7.7 Dispensers (in accordance with ISO 8655-5)

7.7.1 Preparation

Carry out the test by delivery into the weighing vessel (see 7.1.3). Carefully clean the weighing vessel and add a small quantity of test liquid to it. Place the weighing vessel and its test liquid in the balance case. Then place the dispenser under test, with its reservoir already filled with test liquid as near to the balance as possible. Leave both for at least 2 h to come to equilibrium.

7.7.2 Test procedure

After making a first delivery to waste, wipe off any droplets that may have formed on the dispensing nozzle (similar to the handling of piston pipettes) and refill the dispenser in accordance with the supplier's instructions.

NOTE Due to the large effect of piston speed on the measuring result, any information contained in the operation manual regarding piston speed is particularly important (e.g. selection of the speed appropriate for water with power-driven apparatus).

During operation, ensure that the piston does not hit the stroke limits too quickly which could provoke a brief opening of the spring-loaded exhaust valve (spitting caused by the recoil force of the abruptly interrupted flow).

For multiple delivery dispensers (see ISO 8655-5), do not reset the piston between each of the 10 test cycles to its initial position if there is sufficient test liquid remaining to deliver the next test dose.

Use the 10 volumes subsequently dispensed into the weighing vessel to determine the systematic and random errors of measurement (see clause 8).

8 Evaluation

8.1 Calculation of mass loss

Where a mass loss has been determined to enable a correction to be applied for evaporation of the test liquid from the weighing vessel during the test cycle, calculate the mass loss per cycle by using either $(m_{10} - m_{11})/10$ (see 7.2.6 and 7.2.8 for piston pipettes) or by another appropriate method or formula, e.g. specified by the supplier.

8.2 Calculation of the corrected mass of each quantity delivered

If the tare facility of the balance has not been used, calculate the mass of each delivered quantity m_i by subtraction $m_1 - m_0$, $m_2 - m_1$, ..., $m_{10} - m_9$. Add the mass value of the loss per cycle calculated in 8.1 to each delivered quantity m_i.

8.3 Conversion of the corrected mass to volume

The values m_i obtained in accordance with 8.2 are balance readings. A correction taking into account water density and air buoyancy is necessary for the conversion of the balance readings m_i to volumes V_i. The Z correction factors specified in annex A, Table A.1, shall be applied for conversion.

NOTE The Z correction factors given in Table A.1 take into account water density and air buoyancy during weighing at the corresponding test temperature.

Convert each mass m_i obtained from 8.2 by applying the Z correction factors from Table A.1 at the mean temperature and barometric pressure measured in 7.1.4 and using equation (1):

$$V_i = m_i \cdot Z \tag{1}$$

Add together the 10 volumes ($n = 10$) delivered V_i and divide the sum by 10 to provide the mean volume $\overline{V}$ delivered at the test temperature. This value can be expressed in microlitres or millilitres:

$$\overline{V} = \frac{1}{10} \times \sum_{i=1}^{n} V_i \tag{2}$$

If the test temperature is different from the temperature of adjustment (which is 20 °C, see ISO 8655-2, ISO 8655-3, ISO 8655-4 and ISO 8655-5) and if the thermal expansion correction factor Y of the piston-operated volumetric apparatus is known, equation (1) may be replaced by equation (3):

$$V_i = m_i \cdot Z \cdot Y \tag{3}$$

See ISO/TR 20461 for further details.

8.4 Systematic error of measurement

8.4.1 Calculation

Calculate the systematic error e_s of the piston-operated volumetric apparatus in microlitres using equation (4):

$$e_s = \overline{V} - V_s \tag{4}$$

or in percent using equation (5):

$$e_s = 100 \left(\overline{V} - V_s \right) / V_s \tag{5}$$

where V_s is the selected test volume.

In the case of fixed-volume piston-operated volumetric apparatus, the test volume V_s is the nominal volume V_0 and V_s can be replaced by V_0.

8.4.2 Conformity evaluation

The maximum permissible errors specified in parts 2 to 5 of ISO 8655 always apply to every selectable volume of the useful volume range of a piston-operated volumetric apparatus (see e.g. ISO 8655-2:2002, 7.4). In the case of fixed-volume piston-operated volumetric apparatus, where the tested volume V_s is identical with the nominal volume V_0 $(V_s = V_0)$, the values obtained from equation (4) or (5) may be compared directly with the absolute or relative maximum permissible systematic errors specified in parts 2 to 5 of ISO 8655 and shall not exceed these specified values.

However, in the case of variable-volume piston-operated volumetric apparatus, and if the relative systematic error of measurement is used for conformity evaluation, V_s in the denominator of equation (5) shall be replaced by V_0 and the following equation (6) shall be used to compare the relative value obtained, expressed as a percentage, with the specified value in parts 2 to 5 of ISO 8655:

$$e_s = 100\left(\overline{V} - V_s\right)/V_0 \tag{6}$$

8.5 Random error of measurement

8.5.1 Calculation

Calculate the random error of piston-operated volumetric apparatus as the repeatability standard deviation s_r using equation (7):

$$s_r = \sqrt{\frac{\sum_{i=1}^{n}\left(V_i - \overline{V}\right)^2}{n-1}} \tag{7}$$

where n is the number of measurements, in this case $n = 10$.

This random error can also be expressed as a percentage, by the coefficient of variation, CV, using equation (8):

$$\mathrm{CV} = 100\,\frac{s_r}{\overline{V}} \tag{8}$$

8.5.2 Conformity evaluation

In the case of fixed-volume piston-operated volumetric apparatus, where $V_s = V_0$, the values obtained from equation (7) or (8) may be compared directly with the absolute or relative maximum permissible random errors specified in parts 2 to 5 of ISO 8655 and shall not exceed these specified values.

However, in the case of variable-volume piston-operated volumetric apparatus, and if the relative random error of measurement is used for conformity evaluation, equation (8) shall be replaced by equation (9):

$$\mathrm{CV} = 100\,\frac{s_r}{\overline{V}} \times \frac{V_s}{V_0} \tag{9}$$

8.6 Uncertainty of measurement

The uncertainty of measurement u may be assessed in accordance with annex B or ISO/TR 20461.

9 Test report

At least the following information shall be reported:

a) identification of the piston-operated volumetric apparatus by

— supplier's name,

— type name or model number,

— serial number,

— nominal volume or useful volume range;

b) basis of adjustment (Ex) or (In) and reference temperature (20 °C);

c) identification of the type of tip and other consumable accessories used with the piston-operated volumetric apparatus for the test;

d) test conditions under which the test was performed, including temperature, barometric pressure and relative humidity of the test room;

e) reference to the test procedures according to this part of ISO 8655 or alternative test method;

f) systematic and random errors obtained for the test volumes;

g) date of test;

h) identification of operator performing the test.

Annex A
(normative)

Calculation of volumes from balance readings

Values for Z correction factors are given in Table A.1. Z correction factors may also be calculated from equation (3) in ISO/TR 20461:2000.

Table A.1 — Z correction factors for distilled water as a function of test temperature and air pressure

Z values in microlitres per milligram

Temperature °C	**Air pressure** kPa						
	80	**85**	**90**	**95**	**100**	**101,3**	**105**
15,0	1,001 7	1,001 8	1,001 9	1,001 9	1,002 0	1,002 0	1,002 0
15,5	1,001 8	1,001 9	1,001 9	1,002 0	1,002 0	1,002 0	1,002 1
16,0	1,001 9	1,002 0	1,002 0	1,002 1	1,002 1	1,002 1	1,002 2
16,5	1,002 0	1,002 0	1,002 1	1,002 1	1,002 2	1,002 2	1,002 2
17,0	1,002 1	1,002 1	1,002 2	1,002 2	1,002 3	1,002 3	1,002 3
17,5	1,002 2	1,002 2	1,002 3	1,002 3	1,002 4	1,002 4	1,002 4
18,0	1,002 2	1,002 3	1,002 3	1,002 4	1,002 5	1,002 5	1,002 5
18,5	1,002 3	1,002 4	1,002 4	1,002 5	1,002 5	1,002 6	1,002 6
19,0	1,002 4	1,002 5	1,002 5	1,002 6	1,002 6	1,002 7	1,002 7
19,5	1,002 5	1,002 6	1,002 6	1,002 7	1,002 7	1,002 8	1,002 8
20,0	1,002 6	1,002 7	1,002 7	1,002 8	1,002 8	1,002 9	1,002 9
20,5	1,002 7	1,002 8	1,002 8	1,002 9	1,002 9	1,003 0	1,003 0
21,0	1,002 8	1,002 9	1,002 9	1,003 0	1,003 1	1,003 1	1,003 1
21,5	1,003 0	1,003 0	1,003 1	1,003 1	1,003 2	1,003 2	1,003 2
22,0	1,003 1	1,003 1	1,003 2	1,003 2	1,003 3	1,003 3	1,003 3
22,5	1,003 2	1,003 2	1,003 3	1,003 3	1,003 4	1,003 4	1,003 4
23,0	1,003 3	1,003 3	1,003 4	1,003 4	1,003 5	1,003 5	1,003 6
23,5	1,003 4	1,003 5	1,003 5	1,003 6	1,003 6	1,003 6	1,003 7
24,0	1,003 5	1,003 6	1,003 6	1,003 7	1,003 7	1,003 8	1,003 8
24,5	1,003 7	1,003 7	1,003 8	1,003 8	1,003 9	1,003 9	1,003 9
25,0	1,003 8	1,003 8	1,003 9	1,003 9	1,004 0	1,004 0	1,004 0
25,5	1,003 9	1,004 0	1,004 0	1,004 1	1,004 1	1,004 1	1,004 2
26,0	1,004 0	1,004 1	1,004 1	1,004 2	1,004 2	1,004 3	1,004 3
26,5	1,004 2	1,004 2	1,004 3	1,004 3	1,004 4	1,004 4	1,004 4
27,0	1,004 3	1,004 4	1,004 4	1,004 5	1,004 5	1,004 5	1,004 6
27,5	1,004 5	1,004 5	1,004 6	1,004 6	1,004 7	1,004 7	1,004 7
28,0	1,004 6	1,004 6	1,004 7	1,004 7	1,004 8	1,004 8	1,004 8
28,5	1,004 7	1,004 8	1,004 8	1,004 9	1,004 9	1,005 0	1,005 0
29,0	1,004 9	1,004 9	1,005 0	1,005 0	1,005 1	1,005 1	1,005 1
29,5	1,005 0	1,005 1	1,005 1	1,005 2	1,005 2	1,005 2	1,005 3
30,0	1,005 2	1,005 2	1,005 3	1,005 3	1,005 4	1,005 4	1,005 4

Annex B
(informative)

Assessment of the uncertainty of the delivered volume

The calibration of a piston-operated liquid-dispensing apparatus suffers from two sources of uncertainty:

— the uncertainty of the delivery process itself, related to the apparatus;

— the uncertainty of measurement of the delivered volume by the gravimetric method.

According to the GUM (see reference [1] in the Bibliography), both contributions have to be considered for the evaluation of the combined uncertainty of the calibration. Such an evaluation may be required to satisfy a quality assurance protocol.

Experience shows that the contribution to the evaluation of uncertainty resulting from the volume measurement by gravimetric measuring apparatus is small compared to that resulting from the delivery process, provided that measuring instruments (balance, barometer, thermometer, etc.) are used in accordance with the specifications given in this International Standard. Thus, it is good practice to neglect this contribution to the evaluation of uncertainty, and to give only the systematic and random errors of measurement resulting from a tenfold measurement of the delivered volume to characterize the delivering device.

It should be borne in mind that the systematic error of measurement does not influence the evaluation of the uncertainty of the volume measured gravimetrically. It is the result of the measurement, together with its random error, which is the measure characterizing the volume dispensed by the dispensing apparatus.

Under the above-mentioned conditions, the following simplified equation can be used, e.g. for piston pipettes, to assess the uncertainty u of the delivered volume at the 95 % confidence level:

$$u = |e_\mathrm{s}| + 2s_\mathrm{r} \qquad \text{(B.1)}$$

If a more detailed consideration is necessary, e.g. for very small volumes or for delivering apparatus with very high precision, this simplification is no longer valid, and a complete evaluation of the combined uncertainty has to be made. A detailed description of this procedure is given in ISO/TR 20461.

Bibliography

[1] *Guide to the Expression of Uncertainty in Measurement (GUM)*, BUIPM, IEC, IFCC, ISO, INPAC, INPAP and OIML

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