INTERNATIONAL STANDARD

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Piston-operated volumetric apparatus —

Part 7: Non-gravimetric methods for the assessment of equipment performance

Appareils volumétriques à piston —

Partie 7: Méthodes non gravimétriques pour l'estimation de la performance d'équipement

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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 2.

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

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

ISO 8655-7 was prepared by Technical Committee ISO/TC 48, *Laboratory glassware and related apparatus*, Subcommittee SC 6, *Laboratory and volumetric ware*.

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*

— *Part 7: Non-gravimetric methods for the assessment of equipment performance*

Introduction

The ISO 8655 series was developed in order to specify the differing types of piston-operated volumetric apparatus and to provide a reference method and alternative test methods for verifying their characteristics covering the volume range typically from:

— the smallest hand-held pipetting devices, e.g. 1 µl, up to

— the largest laboratory bench-standing volume dispensing instruments, e.g. 100 ml.

ISO 8655-1 provides general requirements and terminology. The detailed volumetric ranges for each type of apparatus specified in the ISO 8655 series are indicated in the appropriate tables of maximum permissible error, i.e. for piston pipettes (ISO 8655-2), for piston burettes (ISO 8655-3), for dilutors (ISO 8655-4) and for dispensers (ISO 8655-5).

ISO 8655-6 is the reference method for type testing and conformity testing. It is gravimetric and contains precise instructions designed to limit variation in procedure and thereby the potential for sources of error – a necessity for type and conformity testing.

The photometric and titrimetric methods described in this part of ISO 8655, are deliberately given as outline methods (see examples in the informative annexes), so that individual laboratories having their own equipment available, and working to different uncertainty requirements, may adapt either these methods, or the gravimetric method, accordingly. If the laboratories operate under ISO 9000 series regimes, or have accreditation to ISO 17025, the individually-adapted methods are usually validated to give results equivalent to those given by the gravimetric method specified in ISO 8655-6.

This part of ISO 8655 is applicable to the following types of testing:

— of piston-operated volumetric apparatus for purposes other than type testing or the conformity testing which is required prior to declarations or certification of conformity;

— in user locations, where there may be no suitable balance or facilities to perform the reference method given in ISO 8655-6, but which may have at their disposal a suitable photometer or automatic titrator.

As users have expressed the wish to have alternative tests available, the following observations are given to help them select the most appropriate test methods for their purposes.

a) **Gravimetric method:** Uncertainty values can increase at volumes significantly below 1 µl, due to increasing balance uncertainty, especially in low humidity areas (where there is increased risk of evaporation) and due to the effects of static electricity. These effects are compensated for through the careful design of the test method specified in ISO 8655-6, which applies to the volume ranges specified in ISO 8655-2 to ISO 8655-5.

b) **Photometric method:** This may be the method of choice for laboratories having a UV/VIS photometer of suitable wavelength and bandwidth. Uncertainty with this method tends to become lower as test volumes decrease and can be further reduced if the volumes used in dilution steps for the preparation of comparative standards use larger capacity Class A glassware (e.g. 100 ml of chromophore solution diluted to 1 000 ml can lead to lower uncertainty than 10 ml diluted to 100 ml).

c) **Titrimetric method:** This may be the method of choice of a laboratory already having a titrator with the properties specified in 6.2 and C.4.1. in Annex C. The method is most suited to the testing of piston-operated volumetric apparatus working in the volume range above 500 µl. Again, uncertainty can be reduced if larger capacity Class A volumetric apparatus and larger weights of solid reagents are used to prepare standard solutions.

If any of these methods is adapted, the expanded uncertainty of measurement needs to be calculated to enable comparison with the reference method. In any case, users will determine that the uncertainty of the chosen method is suitable for their intended purpose.

The tests specified in the ISO 8655 series are intended to be carried out by trained personnel.

Piston-operated volumetric apparatus —

Part 7: Non-gravimetric methods for the assessment of equipment performance

WARNING — The use of this part of ISO 8655 may involve hazardous materials, operations and equipment. This standard does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this part of ISO 8655 to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This part of ISO 8655 specifies the photometric and titrimetric determination of errors of measurement of piston-operated volumetric apparatus. 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 delivery process.

These non-gravimetric test methods can be applied

— as aids to quality assurance by the supplier,

— as routine quality assurance and routine calibrations by the user, and

— as routine and post-repair testing.

The methods described in this part of ISO 8655 are not applicable as alternatives to the gravimetric reference test methods specified in ISO 8655-6, which gives the only method suitable as a basis for supplier's declarations or independent certification of conformity.

NOTE 1 Metrological requirements for piston-operated volumetric apparatus, especially maximum permissible errors, are specified in ISO 8655-2 to ISO 8655-5.

NOTE 2 For conformity tests or type tests for declaration and certification of conformity, see the gravimetric reference test methods in ISO 8655-6.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 648, *Laboratory glassware — One-mark pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

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

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

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

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

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

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

ISO 8655-6:2002, *Piston-operated volumetric apparatus — Part 6: Gravimetric methods for the determination of measurement error*

3 Terms and definitions

For the purposes of this part of ISO 8655, the terms and definitions given in ISO 8655-1 apply.

4 Principle

4.1 Photometric method

The photometric method of testing piston-operated volumetric apparatus relies upon the relationship between the concentration of a chromophore in solution and its absorbance of light at a specified wavelength, as described by the Beer-Lambert law. The method can use one of two procedures, depending on the needs of the calibration. In both methods, the test volume of liquid to be measured is delivered by the piston-operated volumetric apparatus under test into a known volume of liquid, and the degree of dilution is calculated from photometric measurements.

The first method is suitable for test volumes $>$ 20 % of the total volume. The total volume depends on the size of the photometric measuring cell and shall be large enough to adequately fill the cell in the UV/VIS photometer. In this method a known volume of solution is prepared having an absorbance near the upper end of the working range of the photometer and its absorbance is measured. The piston-operated volumetric apparatus being tested is used to add an unknown volume of diluent, e.g. water or buffer. The resulting solution is mixed well and its absorbance is measured. The unknown volume delivered can be calculated from the decrease in absorbance.

The second method is suitable for test volumes $<$ 20 % of the total volume. In this method a known volume of diluent is prepared. The piston-operated volumetric apparatus being tested is used to add an unknown volume of a sample solution of chromophore having known absorbance. The resulting solution is mixed well and its absorbance is measured. The unknown volume delivered is then calculated from the increase in absorbance. Annex A and Annex B give examples for test procedure and calculation.

Other photometric methods can be used, the suitability of which has been validated for the intended purpose.

4.2 Titrimetric method

The titrimetric test method is suitable for testing volumes of piston-operated volumetric apparatus $\geqslant$ 500 µl. In general, any titration can be used, the suitability of which has been validated for the intended purpose.

For example, a potassium chloride (KCl) solution can be used as test liquid to be dispensed by the device under test into an acidified receiver liquid. The resulting test solution is titrated with silver nitrate ($AgNO_3$) solution. The equivalence point is determined by potentiometric detection, e.g. with a silver electrode.

If the device under test is a piston burette, known concentrations of potassium chloride in a receiver vessel can be titrated potentiometrically with silver nitrate using the piston burette under test.

Annex C gives an example for the test procedure.

5 Reagents

All components of reagent solutions shall be of recognized analytical composition and purity.

5.1 Reagents for photometric method

If stock solutions are to be stored for any length of time, they shall be tested for chemical stability, and preservatives added, if needed, to prevent microbiological growth. If the reagents degrade when exposed to light, they shall be stored suitably protected to prevent degradation.

NOTE Instability of reagents when exposed to light can be a major source of uncertainty and a determination of degradation can be necessary.

5.1.1 Water, complying with grade 1 in accordance with ISO 3696.

5.1.2 Chromophore solution

The dispensing characteristics of the chromophore solution, which are influenced by material parameters such as surface tension, density and viscosity, shall be as close as possible compared to those of water in order to facilitate correlation between the photometric and the gravimetric test methods. The potential for adsorption of the chromophore on the wall shall be considered. If a discrepancy between the dispensing properties of the chromophore solution and water is noted during the correlation study of the method, that discrepancy shall be included in the uncertainty analysis.

The chromophore chosen shall be completely soluble at the highest concentration required.

NOTE Suitable chromophores are 2,2-azino-di-[3-ethylbenzthiazoline sulfonate(6)] (ABTS, relative molecular mass M_r = 547,7), potassium dichromate $K_2Cr_2O_7$, Ponceau S and Orange G. An example of a reagent system based on Ponceau S is given in Annex A.

5.1.3 Reagent system

The reagent system, consisting of chromophore, diluent, preservative (if needed) and buffer (if needed) shall be chosen with the following criteria in mind. In all cases the uncertainty of measurement due to the various contributions, e.g. uncertainty of pH, shall be estimated and included in the uncertainty budget.

NOTE An example is given in ISO/TR 16153 [1].

The concentration against absorbance relationship for the reagent system shall be well documented in literature or shall be determined by the user. The wavelength chosen for absorbance measurement shall be at or near an absorbance maximum of the reagent system to minimize the effect of wavelength errors on results.

The reagent system shall either be independent of pH or be buffered to limit pH change to an acceptable range established in the uncertainty budget.

The reagent system shall either be independent of temperature or the results shall be characterized and compensated for temperature.

5.1.4 Reagent solutions, to be prepared in concentrations depending on the volumes to be tested.

5.2 Reagents for titrimetric method

If the titration of potassium chloride with silver nitrate is used as the titrimetric method, solutions in accordance with 5.2.1 to 5.2.4 shall be used.

5.2.1 Water, complying with grade 1 in accordance with ISO 3696.

5.2.2 Nitric acid, $c(HNO_3)$ = 1 mol/l or **sulfuric acid** $c(H_2SO_4)$ = 0,5 mol/l.

5.2.3 Potassium chloride standard solutions, c(KCl) = 1 mol/l, c(KCl) = 0,1 mol/l and c(KCl) = 0,01 mol/l.

5.2.4 Silver nitrate standard solution, $c(AgNO_3)$ = 0,1 mol/l.

The solution shall be stored protected from light.

6 Apparatus

All apparatus shall be chosen such that the required uncertainty of measurement can be obtained. An example of the calculation of the expanded uncertainty of a photometric method is given in ISO/TR 16153 [1].

All equipment shall be traceable to international or national standards and be of suitable readability, accuracy, reproducibility and stability, consistent with the required expanded uncertainty of measurement.

6.1 Photometric method

6.1.1 UV/VIS photometer, with adequate resolution, linearity, repeatability, bandpass, absorbance accuracy and wavelength accuracy over the range of absorbances utilized in the method.

An example is given in A.4.1 and Table A.3.

6.1.2 Measuring cell, with suitable optical quality.

If its pathlength is not known with sufficient accuracy to meet the requirements of the expanded uncertainty, then a second reagent with known concentrations and absorptivity can be used to enable calculation to compensate for the pathlength's influence on results.

An example is given in A.4.2.

A ratiometric analysis can be applied to determine the unknown volume without reference to measuring cell pathlength.

6.1.3 Thermometer

If results are temperature-dependent, the temperature of the solutions shall be measured using a thermometer with uncertainty consistent with the expanded uncertainty of the measurement.

6.1.4 Volumetric glassware, Class A

Known volumes of diluent or reagent solutions may be prepared either by using Class A volumetric glassware, or by weighing, in which case the densities of the solutions shall be known.

If piston-operated volumetric apparatus is used for preparation of solutions, it shall conform to the applicable part of ISO 8655 (see Clause 2) and shall be calibrated in accordance with ISO 8655-6.

6.2 Titrimetric method

6.2.1 Complete titration equipment, comprising burette, e.g. in accordance with ISO 8655-3, and a sensor system for detection of the equivalence point of the chosen titration.

6.2.2 Electrode

If the titration of potassium chloride with silver nitrate is used as the titrimetric method, a combined silver electrode should be used for potentiometric indication of the equivalence point. The silver surface of the electrode should, preferably, be coated with AgCl or Ag_2S (see C.4.2).

6.2.3 Class A volumetric glassware, such as one-mark pipettes in accordance with ISO 648 and one-mark volumetric flasks in accordance with ISO 1042.

If piston-operated volumetric apparatus is used for the preparation of solutions, it shall conform to the applicable part of ISO 8655 (see Clause 2) and shall be calibrated in accordance with ISO 8655-6.

6.2.4 Analytical balance

If the standard solutions according to 5.2.3 and 5.2.4 are prepared by the user, an analytical balance with appropriate performance, such as appropriate minimum mass, shall be used.

7 Test conditions

7.1 Test room and general conditions should be in accordance with 6.1 and 6.2 of ISO 8655-6:2002.

7.2 Testing volume and number of measurements per volume to be tested depend upon user requirements. Guidance can be found in 7.1.1 and 7.1.2 of ISO 8655-6:2002.

8 Procedure

8.1 General

Perform the preparation of solutions and measurements at a stable temperature, preferably 20 °C.

Perform the testing in accordance with the general principles specified in 4.1 and 4.2, and in accordance with the manufacturer's instructions for the equipment specified in 6.1 and 6.2.

8.2 Photometric method

Two detailed examples for the application of the photometric method, including calculation of the dispensed testing volumes, are given in Annexes A and B. In the first example, a removable measuring cell (also known as cuvette or vial) containing a known volume of diluent is placed into the UV/VIS photometer and the test volume is dispensed into it while it is in the UV/VIS photometer. The absorbance of the mixture is read after mixing.

In the second example (see Annex B), the test volume is dispensed into a container with a known volume of diluent, the solution is mixed, and an aliquot is drawn into a flow cell in a UV/VIS photometer where the absorbance is measured.

In both cases the unknown volume is calculated using the Beer-Lambert law, based on measured absorbances and the diluent volume.

8.3 Titrimetric method

A detailed example for the application of the titrimetric method, including calculation of the dispensed testing volumes, is given in Annex C. If the titration of potassium chloride with silver nitrate is used as the titrimetric method, solutions shall be chosen as specified in Table 1. Water for the preparation of all solutions shall comply with ISO 3696, grade 1.