



BSI Standards Publication

Determination of uncertainty for volume measurements of a piston-operated volumetric apparatus using a photometric method

National foreword

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Determination of uncertainty for volume measurements of a piston- operated volumetric apparatus using a photometric method

*Détermination de l'incertitude de mesure pour les mesurages
volumétriques des appareils volumétriques à piston au moyen de la
méthode photométrique*





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ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 48, *Laboratory equipment*.

This second edition cancels and replaces the first edition (ISO/TR 16153:2004), which has been technically revised.

The main changes are as follows:

- the term “standard deviation of the mean delivered volume” has been replaced in this document by “repeatability” according to ISO/IEC Guide 99 (VIM);
- a new uncertainty calculation example has been supplied;
- new uncertainty components have been added, namely, reproducibility, air cushion and resolution;
- new [Annex A](#) concerning the uncertainty in use of a single delivered volume has been added;
- new [Annex B](#) concerning volume correction due to pressure changes has been added.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The example given in this document is informative and supports the requirements found in [ISO 8655-8:2022](#), 9.4 and [ISO 8655-7:2022](#), 4.2, to perform an estimation of measurement uncertainty when calibrating POVA according to the measurement procedures described in these documents and the principles of ISO/IEC Guide 98-3.

The revision of this document coincides with a major revision of the ISO 8655 series in 2022, reflecting the state-of-the-art measurement procedures and approaches for the estimation of measurement uncertainty.

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Determination of uncertainty for volume measurements of a piston-operated volumetric apparatus using a photometric method

1 Scope

This document gives detailed information regarding the evaluation of uncertainty for the photometric reference measurement procedure specified in [ISO 8655-8](#) and the photometric procedure specified in [ISO 8655-7:2022](#), Annex B according to ISO/IEC Guide 98-3.

This document also describes the determination of other uncertainty components related to the liquid delivery process of a piston-operated volumetric apparatus (POVA), e.g. repeatability and handling. Furthermore, it provides examples for the calculation and application of the uncertainty of the mean delivered volume and the uncertainty in use of a single delivered volume.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 8655-1](#), *Piston-operated volumetric apparatus — Part 1: Terminology, general requirements and user recommendations*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in [ISO 8655-1](#) apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

4 Modelling the measurement

The dual-dye ratiometric photometric measurement procedures described in [ISO 8655-7](#) and [ISO 8655-8](#) use a cuvette containing a copper(II) chloride solution of known volume, which is determined by a gravimetric method. The POVA under test is used to add an unknown volume of test solution with known Ponceau S concentration to the cuvette containing CuCl_2 solution. The contents of the cuvette are mixed without removing the cuvette from the light path of the spectrophotometer, and absorbances at 520 nm and 730 nm are measured before and after the addition of test solution.

Calibrator solutions of CuCl_2 and Ponceau S are prepared, and their absorbance values at 520 nm and 730 nm measured. Preparation of the Ponceau S test solutions of different concentrations involves the preparation of dilutions, which are expressed by the dilution ratio, R . Absorbances of the calibrator solutions, together with the dilution ratio, R , are used to calculate the calibration constant, K , for a given concentration of Ponceau S.

The unknown volume of Ponceau S solution delivered by the POVA under test is calculated from the volume and absorbances of the CuCl_2 solution prior to addition of test solution, the calibration constant K , and the absorbance of the mixture in the cuvette after addition of test solution.

The Formula for the total volume $V_T(i)$ of delivered test solution after the i -th delivery at the test temperature is given by [Formula \(1\)](#):

$$V_T(i) = V_{C0} \frac{\frac{A_{M520}(i) - A_{C520}}{A_{C730} - A_{C520}}}{K_j - \frac{A_{M520}(i) - A_{C520}}{A_{C730} - A_{C520}}} \quad (1)$$

where

$V_T(i)$	is the total volume of test solution which has been added to the test cuvette from the first delivery through the i -th delivery;
V_{C0}	is the actual volume of copper(II) chloride solution in the prepared test cuvette at the start of the test;
K_j	is the calibration constant from Formula (2) ;
$A_{M520}(i)$	is the absorbance at 520 nm of the cuvette mixture after the i -th delivery of test solution;
A_{C520}	is the absorbance at 520 nm of the copper(II) chloride solution in the cuvette prior to the first delivery of test solution;
A_{C730}	is the absorbance at 730 nm of the copper(II) chloride solution in the cuvette prior to the first delivery of test solution.

The calibration constant (K_j) for each batch of solutions is calculated using [Formula \(2\)](#). Absorbance values are obtained from the measurements in [ISO 8655-8:2022](#), 8.2.

$$K_j = \frac{1}{R_j} \left(\frac{A_{Cal520j} - A_{CalC520}}{A_{CalC730} - A_{CalC520}} \right) \quad (2)$$

where

K_j	is the calibration constant for the test-volume-specific calibrator solution [the subscript j refers to the test volume (V_S)];
R_j	is the dilution ratio of the calibrator solution;
$A_{Cal520j}$	is the absorbance of the Ponceau S calibrator solution j at 520 nm;
$A_{CalC520}$	is the absorbance of the CuCl_2 solution at 520 nm;
$A_{CalC730}$	is the absorbance of the CuCl_2 solution at 730 nm.

The dilution ratio (R) is calculated according to [Formula \(3\)](#).

$$R = \frac{V_{PS}}{V_{PS} + V_C} \quad (3)$$

where

R	is the dilution ratio;
V_{PS}	is the actual measured volume of Ponceau S solution;
V_C	is the actual measured volume of copper(II) chloride solution.

[Formulae \(1\)](#), [\(2\)](#) and [\(3\)](#) contain nine input variables. Six of these inputs are photometric absorbance values. Three inputs are liquid volumes at the test temperature and each of these three volumes is determined by weighing on a balance.

The liquid volumes V_{C0} , V_{PS} and V_C at the test room temperature are calculated according to [Formula \(4\)](#).

$$V_L = (m_L - m_E) \times \frac{1}{\rho_L - \rho_A} \times \left(1 - \frac{\rho_A}{\rho_B} \right) \quad (4)$$

where

- V_L is the calculated volume at the temperature of the test liquid, in ml;
 m_L is the balance indication of the weighing vessel after liquid delivery, in g;
 m_E is the balance indication of the weighing vessel before liquid delivery, in g ($m_E = 0$ in case the balance was tared with the weighing vessel);
 ρ_A is the density of air, in g/ml (see [Formula \(5\)](#) below);
 ρ_B is the actual or assumed density of the weights used to calibrate the balance, in g/ml;
 NOTE Stainless steel weights of density 8,0 g/ml are typically used for balance calibration.
 ρ_L is the density of the liquid at the test temperature, in g/ml.

[Formula \(5\)](#) for the air density can be used at temperatures between 15 °C and 27 °C:

$$\rho_A = \frac{1}{1\,000} \times \frac{0,348\,48 \times P - 0,009 \times h_r \times e^{(0,061 \times t)}}{t + 273,15} \quad (5)$$

where

- ρ_A is the air density, in g/ml;
 t is the ambient temperature, in °C;
 P is the barometric pressure, in hPa;
 h_r is the relative air humidity, in %.

The relative uncertainty of [Formula \(5\)](#) is $2,4 \times 10^{-4}$ g/ml under the following conditions: barometric pressure between 600 hPa and 1 100 hPa, ambient temperature between 15 °C and 27 °C, and relative humidity between 20 % and 80 %.

At other environmental conditions, [Formula \(5\)](#) is replaced with the CIPM-2007 calculations described in Reference [3].

According to [ISO 8655-8](#), the mean volume is calculated according to [Formula \(6\)](#):

$$\bar{V} = \frac{V_T(n)}{n} \quad (6)$$

where

- $\bar{V}$ is the mean volume;
 $V_T(n)$ is the total volume of test solution in the cuvette after the n -th delivery (typically, $n = 10$).

If a cubic expansion coefficient γ for the POVA is known, it can be applied to correct the dispensed volume to the reference temperature using [Formula \(7\)](#).

$$V_{T,\text{ref}}(i) = V_T(i) \times [1 - \gamma(t_L - t_{\text{ref}})] \quad (7)$$

where

- $V_{T,\text{ref}}(i)$ is the total volume of test liquid after the i -th delivery corrected to a reference temperature;
 γ is the cubic thermal expansion coefficient for the POVA under test;
 t_L is the temperature of the test liquid at the test room temperature;
 t_{ref} is the reference temperature for the POVA, typically 20 °C or 27 °C.

5 General procedure for the uncertainty calculation

The evaluation of measurement uncertainty in this document follows ISO/IEC Guide 98-3. The method has the following steps:

- a) Expressing, in mathematical terms, the relationship between the measurand and its input quantities