International Standard

ISO 33403

# Reference materials — Requirements and recommendations for use

*Matériaux de référence — Exigences et recommandations pour l'utilisation*



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# Contents

Page

# Foreword

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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).

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This document was prepared by Technical Committee ISO/TC 334, *Reference materials*.

This first edition cancels and replaces ISO Guide 33:2015, which has been technically revised.

The main changes are as follows:

— title modified;

— 1.5 removed;

— 5.3 and 5.4 removed;

— Figure 1 revised and explanation inserted;

— 6.1.4: former Annex A Table A.1 inserted as Table 1;

— 9.1.3 removed;

— 9.2.1 revised;

— 9.3.1 and 9.3.2 revised and merged into 9.3.1

— 10.2.1 moved to 10.1.1 and former 10.1.1. added as 10.1.2;

— 12.2 and 12.3 moved into the new Annex C;

— former Annex B now Annex A;

— former Annex C now Annex B;

— Bibliography revised.

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

This document provides general recommendations on the use of reference materials (RMs). These recommendations are exemplified by real-world examples, which to some degree also reflect the level of complexity associated with RMs. This level of detail is deemed to be useful for users of RMs and anyone who has a responsibility in the quality management in laboratories, e.g. drafters, reviewers, managers and assessors of procedures, working instructions and standard operating procedures.

For certified reference materials (CRMs), the metrological traceability of the property values to international scales or other measurement standards has been established. For RMs that are not CRMs, this kind of traceability of property values has often not been established. Nevertheless, these RMs can still be used for assessing parts of measurement procedures, including evaluating various levels of precision.

Mainstream applications of RMs are listed in 6.1.1. Not all types of RMs can be used for all indicated purposes.

# Reference materials — Requirements and recommendations for use

## 1 Scope

This document describes good practice in using reference materials (RMs), and certified reference materials (CRMs) in particular, in measurement processes. These uses include:

— the assessment of precision and trueness of measurement methods;

— quality control;

— assigning values to materials;

— calibration;

— establishing conventional scales.

This document also relates key characteristics of various types of RMs to the different applications.

The preparation of RMs for calibration is also part of the scope of ISO 17034 and ISO 33405. The treatment in this document is limited to the fundamentals of small-scale preparation of RMs and the value assignment, as used by laboratories to calibrate their equipment. Larger scale production of such RMs, with the possible aim of distribution, is beyond the scope of this document. This type of activity is covered in ISO 17034 and ISO 33405.



## 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 Guide 30, *Reference materials — Selected terms and definitions*

ISO/IEC Guide 99, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

## 3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO Guide 30 and ISO/IEC Guide 99 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 Symbols

| | |
|---|---|
| $\alpha$ | risk of error of the first type (type I error) |
| $\beta$ | risk of error of the second type (type II error) |
| $\chi^2$ | chi-squared |
| $d$ | measurement bias |
| $k$ | coverage factor |
| $s_w$ | standard deviation computed from repeat observations |
| $\sigma_w$ | intralaboratory standard deviation |
| $\sigma_{wo}$ | required intralaboratory standard deviation |
| $u()$ | standard uncertainty of the parameter in parenthesis |
| $U()$ | expanded uncertainty of the parameter in parenthesis |
| $u_{CRM}$ | standard uncertainty associated with property value of the CRM |
| $u_{meas}$ | standard uncertainty associated with value obtained by measuring the CRM |
| $u_{prep}$ | uncertainty associated with the value obtained from preparation of a calibrant |
| $x_{CRM}$ | value of a specified property of the CRM |
| $x_{meas}$ | value obtained by measuring the CRM |
| $x_{prep}$ | value obtained from preparation of a calibrant |
| $\bar{x}$ | average of repeat observations |



# 5 Conventions

In this document, the following conventions are used:

A measurand is specified in such a way that there exists a unique, but unknowable, 'true value'.

All statistical methods used in this document are based on the following assumptions:

a) The certified value is the best estimate of the true value of the property of the CRM.

b) All variation, be it associated with the material (i.e. homogeneity) or the measurement process, is random and follows a normal probability distribution. The values of probabilities stated in this document assume normality. The probability may be different if there is deviation from normality.

Property values that are not certified values are considered to be unfit for use in metrological applications requiring a value assigned to the measurand, such as calibration, or the assignment of values to other materials.

Throughout this document, the law of propagation of uncertainty is used. Other methods of propagating uncertainties can be applied as well, and in some cases such alternative methods are required by the circumstances of the application. Further guidance on these matters is given in ISO/IEC Guide 98-3:2008 and its supplements.

# 6 RMs and their role in measurement

## 6.1 Common applications of RMs

**6.1.1** RMs, and CRMs in particular, are widely used for the following purposes:

— method validation (Clause 8 and Clause 9);

— quality control of a measurement or measurement procedure (Clause 8 and Clause 9);

— establishing metrological traceability (Clause 9, Clause 10 and Clause 11);

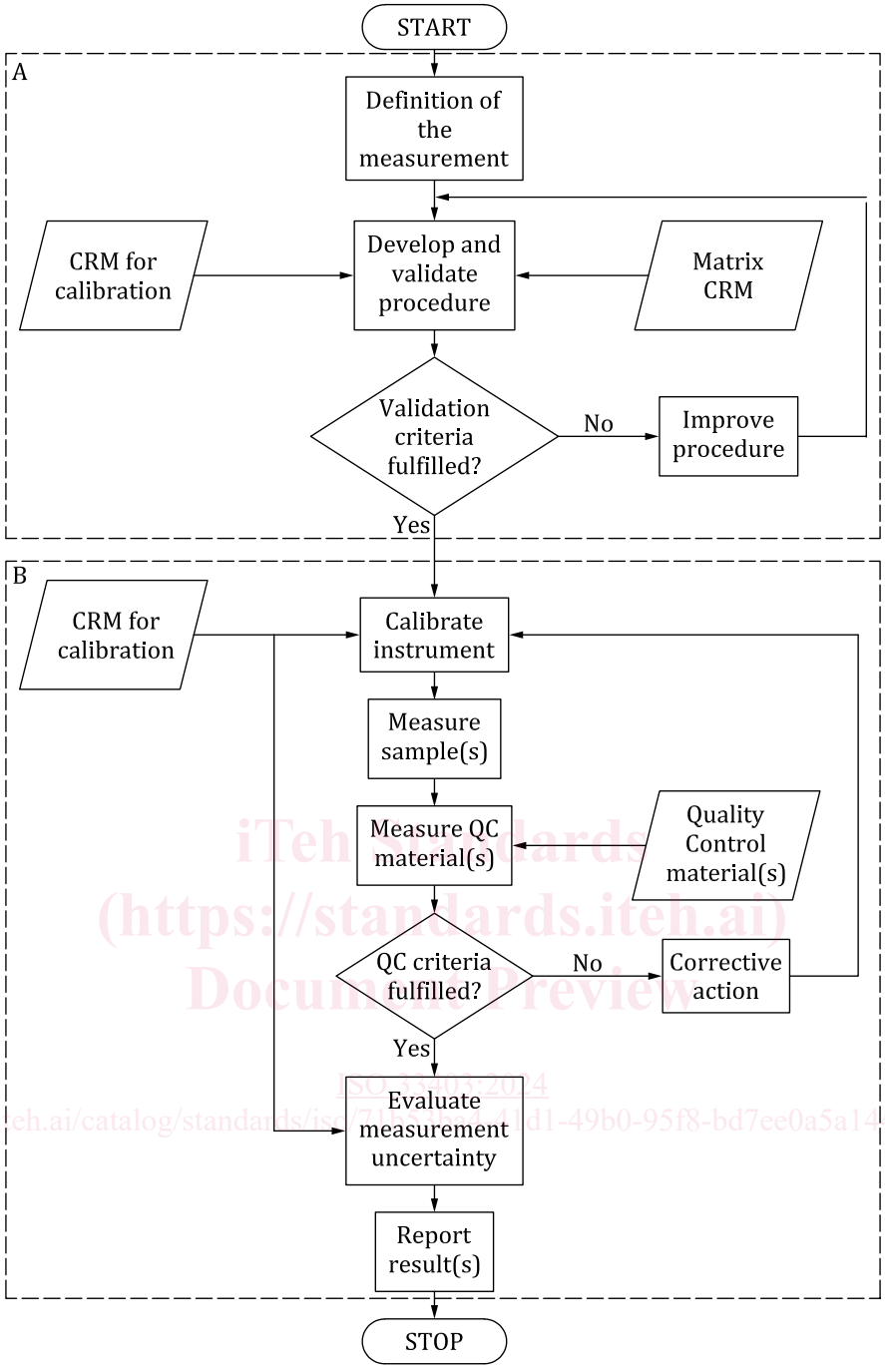
— calibration of equipment or a measurement procedure (Clause 10);

— assigning values to other materials (Clause 11);

— maintaining conventional scales (Clause 12).

Figure 1 presents a schematic of how CRMs can be used in a measurement process. CRMs for calibration are often used to calibrate an analytical instrument. The data from the instrument calibration is usually used to set up a calibration curve that is used for the calculation of the measurement results. The uncertainty from the CRMs that were used for the calibration of the instrument will also be an uncertainty contribution to the uncertainty of the measurement results. Matrix CRMs are often also used for instrument calibration for measurement techniques that analyse solid samples, such as X-ray fluorescence for geological or mineralogical samples or laser ablation inductively coupled plasma mass spectrometry, as well as many other surface analysis techniques.

During method validation, matrix CRMs are usually used to evaluate the measurement trueness of the optimised method. This approach is especially applicable when the matrix of the CRM is a close match to the routine samples being analysed by the laboratory. It is also important to note that the same matrix CRM cannot be used to both calibrate the response of the measurement instrument and evaluate the measurement trueness during method validation.






**Key**

A procedure development and validation

B routine measurement

**Figure 1 — Schematic outline of a measurement and two possible uses of CRMs therein**

**6.1.2** Standards for the general requirements for the competence of laboratories, for example ISO/IEC 17025 and ISO 15189, require measurement results to be metrologically traceable and measurement equipment calibrated. Metrological traceability is a prerequisite for achieving comparable and compatible measurement results.

EXAMPLE A wine with a volume fraction of 12 % alcohol can be usefully compared with another wine with a volume fraction of 13,5 % alcohol.

**6.1.3** It is usually taken for granted that measurement results, expressed in appropriate units, are comparable. In order to meet this implicit expectation of measurement data, laboratories should ensure that all equipment is properly calibrated using measurement standards, which in turn have been made metrologically traceable to the realization of the relevant unit. In many cases, this unit is part of the International System of Units (SI).

**6.1.4** A summary list of key characteristics of RMs, cross-referenced to the common applications of RMs, is given in Table 1.

**Table 1 — Key characteristics of reference materials (RMs) and their relevance in common applications**

| | Assessment of precision | Bias assessment | Calibration/conventional scales | Assigning values to other materials |
|---|---|---|---|---|
| Specification of the property of interest | Required | Required | Required | Required |
| Property value | | Required | Required | Required |
| Stated uncertainty | | Required | Required | Required |
| Specified level of homogeneity | Required | [a] | [a] | [a] |
| Specified level of stability | Required | [a] | [a] | [a] |
| Statement of metrological traceability | | Required | Required | Required |
| Instructions for use | Required | Required | Required | Required |
| Expiry date of the certificate | | Required | Required | Required |

[a] Uncertainty contribution included in the stated uncertainty associated with the property value.



## 6.2 Property values

### 6.2.1 General



**6.2.1.1** CRMs are characterized for one or more properties. These property values are accompanied by:

a) a clear specification of the property concerned;

b) an uncertainty statement;

c) a statement of metrological traceability;

d) a period of validity of the certificate.

The user should verify that all this information is available in an unambiguous form.

**6.2.1.2** Indicative values should not be used for any of the uses of CRMs described in this document.

NOTE The terminology used in practice for indicative values is not always consistent with this document.

### 6.2.2 Specification of the property

**6.2.2.1** The unambiguous specification of the property concerned assists greatly in deciding whether the CRM is appropriate for the user's intended application. The user of a CRM is responsible for assessing the suitability of the material for their own application.

EXAMPLE For trace elements in soil, it is important to specify whether it is the total content, content obtained by incomplete destruction (e.g. aqua regia), leachable content or a particular species containing the trace element.