



**International  
Standard**

**ISO 33403**

**Reference materials —  
Requirements and  
recommendations for use**

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

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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](http://www.iso.org/directives)).

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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](http://www.iso.org/iso/foreword.html).

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](http://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.

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# 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

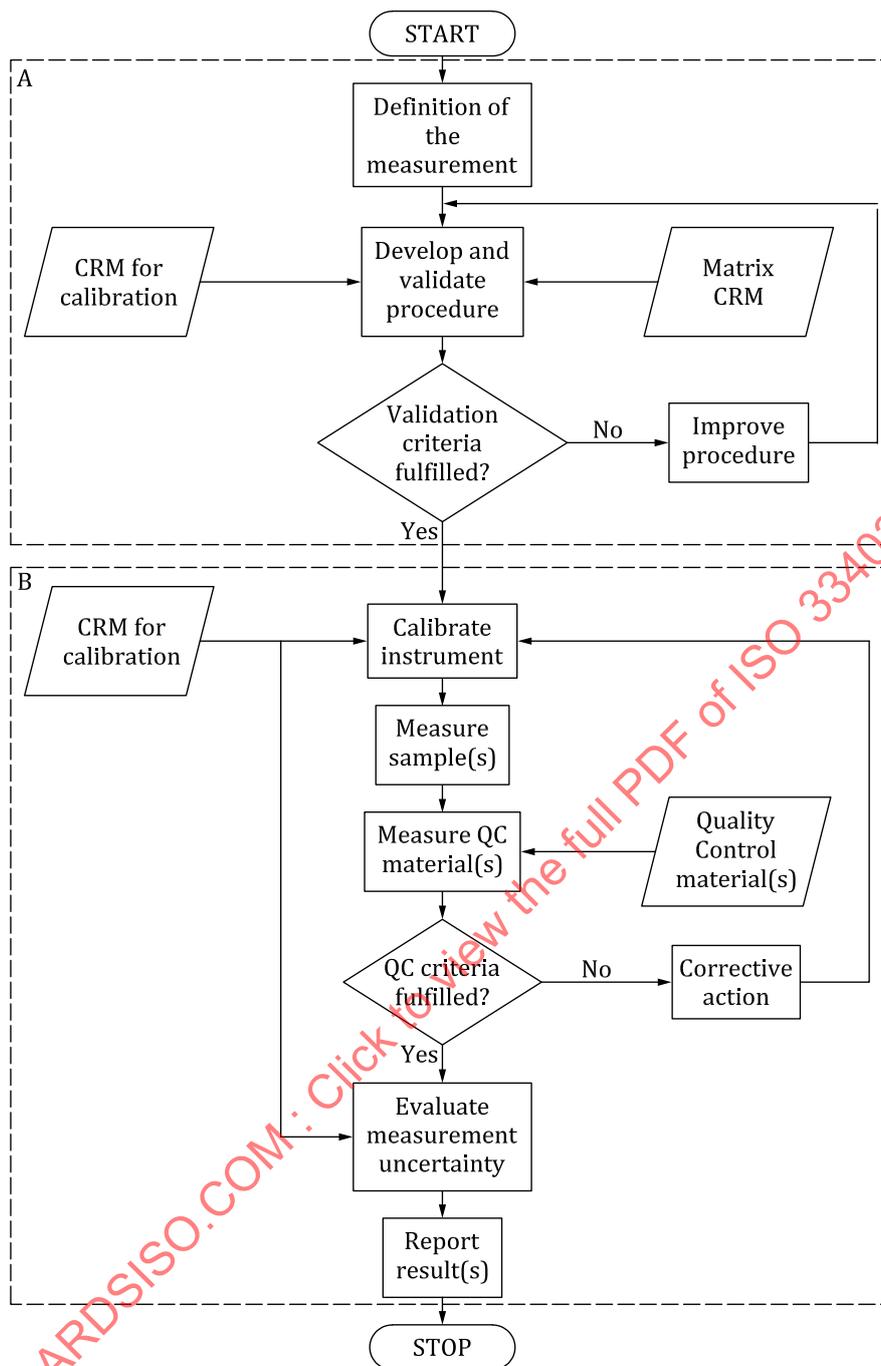
### 6.1 Common applications of RMs

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

<sup>a</sup> 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.

**6.2.2.2** The property values should be given in appropriate units, preferably SI units. The property values should be given in an appropriate number of digits, to prevent unnecessary loss of accuracy on the one hand and to avoid giving a false impression of accuracy on the other.

NOTE ISO/IEC Guide 98-3:2008, Clause 7 gives guidance on the rounding of measurement results and associated uncertainties.

### 6.3 Uncertainty statement

**6.3.1** The uncertainty statement should be readily understood, which among other considerations requires that all information necessary to convert the uncertainty stated into a standard uncertainty is available. If an expanded uncertainty is given, then usually the appropriate coverage factor is sufficient for this conversion.

EXAMPLE A calibration certificate for a gas mixture states the following for the amount of substance fraction of carbon monoxide:

$$x_{\text{CO}} = (41\,122 \pm 28) \mu\text{mol/mol} \quad (k = 2)$$

The expanded uncertainty is 28  $\mu\text{mol/mol}$ . The standard uncertainty is obtained using:

$$u = \frac{U}{k} = \frac{28}{2} = 14 \mu\text{mol mol}^{-1}$$

**6.3.2** If a coverage interval is given, then the (assumed) probability density function of the property value should be specified, including the coverage probability (e.g. 95 %) of the stated interval. Such an interval can be asymmetric. Sometimes, it can be necessary to make additional assumptions concerning, e.g., the appropriate coverage factor. In those cases, the guidance of ISO/IEC Guide 98-3:2008, 6.3 should be followed.

EXAMPLE The carbon content in a gas coal is specified as 760,1 mg/g and the uncertainty is stated as 2,1 mg/g. The following footnote is added to the uncertainty statement: "The uncertainty is expressed as the 95 % confidence interval. It is applicable when the reference material is used for calibration purposes."

From the certification report, it is clear that the certified values have been obtained from an interlaboratory experiment, and therefore it is reasonable to assume the normal distribution. The half-width of a 95 % confidence interval equals 1,96 times the standard deviation. There is, however, no practical difference with using a (coverage) factor of 2, which would correspond to the normal distribution with a 95,45 % confidence level.

The standard uncertainty is obtained using:  $u = \frac{U}{k} = \frac{2,1}{2} = 1,05 \text{ mg g}^{-1}$

**6.3.3** The uncertainties stated should be given in the same unit as the property values or, alternatively, expressed as a fraction of the property value (i.e. as a relative expanded uncertainty). If such fractions are used, it should be established whether the conversion into absolute standard uncertainties can be performed in an unambiguous way.

NOTE Such fractions include percentages, per mil and parts-per-million (ppm), although none of these are recommended for this purpose because of their ambiguity.

**6.3.4** CRMs are accompanied by a certificate stating, among other things, the properties certified, their values and their associated uncertainties (see [6.2.1.1](#)). It is beyond the scope of this document to describe how the uncertainty associated with property values is established, but it is important to understand the potential main contributors.

NOTE Details concerning the establishment of an uncertainty budget for property values are given in ISO 33405.

The main contributors to the uncertainty associated with the property values of a CRM include:<sup>[16]</sup>

— uncertainty from characterization;

- uncertainty due to long-term stability;
- uncertainty due to stability under conditions of transport (often referred to as “short-term stability”), where applicable;
- uncertainty due to heterogeneity between units and where applicable within units (often referred to as “homogeneity”).

**6.3.5** In some cases, detailed knowledge of different parts of the uncertainty budget can be helpful, in particular if such a contribution is the largest. This information can be available from the CRM producer.

**6.3.6** Not all uncertainty statements accompanying the property values on certificates of CRMs produced before the late 1990s include effects of batch inhomogeneity and instability. The uncertainty stated on the certificate should comprise all factors that can impact the scatter of the property value(s) across the batch and over time. Ultimately, the uncertainty stated should be applicable to the single package to be used in the measurement process.<sup>[16]</sup>

NOTE If the uncertainty stated is too small, the expanded uncertainty has a lower level of coverage than stated.

**6.3.7** RMs that do not come with property values should come with some information regarding the (between-bottle) homogeneity and long-term stability of the properties for which the RM can be used. The user should verify whether this information is provided in a form and that it can be used to assess the suitability of the RM. Such assessment may include the use of the information concerning homogeneity and stability in subsequent uncertainty calculations.

## 6.4 Traceability statement

**6.4.1** Metrological traceability is a property of a measurement result. As the value obtained during the characterization of a CRM (the certified value) is a measurement result, it can have this attribute too. A key characteristic of property values of CRMs is that their metrological traceability is established.

**6.4.2** The user of a CRM should verify that the property values come with a statement concerning the metrological traceability of these values. This statement should inform the user about the measurement scale to which these values refer, so they can verify whether the CRM is suitable for the intended use.

NOTE In most cases, the measurement scale is the SI unit.

**6.4.3** To allow interpretation of statements of metrological traceability, the following are necessary and should be stated on a certificate or other documentation accompanying a CRM:

- a) the specification of the measurand;
- b) the unit to which the property value is made traceable;
- c) the method used for sample handling or transformation and measurement procedures(s) or technique(s) used in the characterization;
- d) the approach to characterization (e.g. single method, two methods, multiple laboratories; see ISO 17034).

NOTE Documentation accompanying a CRM can be made available by different means, including websites, email or publications in the open literature.

**6.4.4** The provider of the result of a measurement is responsible for supporting the claim of metrological traceability for that result or value. In the case of CRMs, the producer bears this responsibility. It is the user's responsibility to review the appropriateness of the metrological traceability for their own application.

**6.4.5** For assessing a claim of metrological traceability, the user can require more information than provided on the certificate. A claim of metrological traceability is typically supported by items mentioned in [6.4.3](#).

The user of an RM should scrutinize this information and assess the fitness for purpose of a particular RM for the intended use. The user of the RM should check the availability of the information specified in this clause to assist in the assessment. If essential parts of this information are unavailable, the RM could be unsuitable for an application.

## 7 Handling of RMs and CRMs

**7.1** The instructions for use, as well as those for storage, shall be followed, as they form part of the conditions under which the property values and associated uncertainties are valid. Improper use of RMs and CRMs can be detrimental to the performance of measurement procedures and shall be avoided.

**7.2** The period of validity on the certificate should be respected. The fitness for purpose of the material cannot be guaranteed beyond the period of validity (or expiry date).

**7.3** In particular for CRMs that allow multiple use, users should make sure that the container holding the CRM is properly closed and it is stored in an appropriate manner.

**7.4** The minimum subsample size should be respected. Smaller subsamples can be unrepresentative.

**7.5** Sub-sampling of such CRMs should be done in such a way that the subsample taken for use reflects the properties of the complete package. Otherwise, over time, the remaining material of the CRM will possibly no longer be representative for the batch that has been produced and certified, hence the values and uncertainties stated on the certificate will no longer be valid.

NOTE Re-homogenization of CRMs is usually necessary before sub-sampling can be carried out. Such instructions are typically given in the documentation accompanying the CRM.

So-called “single-shot” CRMs are designed for use as a single portion. Usually, the unit contains sufficient sample for only one or two measurements. However, where single shot materials are designed for use as a single portion, they should not be subdivided.

## 8 Assessment of precision

### 8.1 General

**8.1.1** Checking the precision of a measurement procedure as applied by a laboratory involves comparison of the intralaboratory standard deviation under repeatability conditions (or other specified conditions) and the specified value of that standard deviation.

NOTE Measures of precision are the standard deviation under repeatability or reproducibility conditions.

**8.1.2** Assessment of precision can be part of the activities a laboratory undertakes when developing or validating a method. Such experiments should ideally be run on RMs covering the scope of the method in terms of matrices (or variations within a matrix) and property value levels.<sup>[19]</sup> The assessment may also involve multiple laboratories. More guidance on assessing precision in interlaboratory studies is given in ISO 5725-1, ISO 5725-2, ISO 5725-3, ISO 5725-4, ISO 5725-5 and ISO 5725-6.

**8.1.3** Results from periodic checks of a measurement procedure may be recorded on a quality control chart. A range control chart may also be used for this purpose (see ISO 7870-5).

## 8.2 Number of replicate measurements

**8.2.1** For a reliable assessment of precision within a required confidence interval, the necessary number of replicate measurements can be estimated by a  $\chi^2$  test. The number of replicate measurements,  $n$ , required depends mainly on the values of  $\alpha$  and  $\beta$  and the alternative hypothesis chosen for the assessment of precision. [Annex B](#) gives an explanation of the probabilities  $\alpha$  and  $\beta$  associated with the type I and type II risks in statistical hypothesis testing.

[Table 2](#) shows the relationship between the degrees of freedom  $\nu$  (where, in this case,  $\nu = n - 1$ ) and the ratio of the intralaboratory standard deviation of the measurement process,  $s_w$ , and the specified value of the intralaboratory standard deviation,  $\sigma_{wo}$ , for various values of  $\beta$  at  $\alpha = 0,05$ .

**EXAMPLE** For  $n = 10$ , the probability that the variance of the measurement results will pass the appropriate  $\chi^2$  test (see [8.6](#)) at  $\alpha = 0,05$  is no more than 1 % when the intralaboratory standard deviation,  $\sigma_w$ , of the measurement process is equal to or larger than 2,85 times the specified value of  $\sigma_{wo}$ .

**Table 2 — Ratio of the standard deviation of the measurement process to the specified value for various values of  $\beta$  and degrees of freedom  $\nu$  at  $\alpha = 0,05$**

$\nu$	$\alpha = 0,05$			
	$\beta = 0,01$	$\beta = 0,05$	$\beta = 0,1$	$\beta = 0,5$
1	159,5	31,3	15,6	2,73
2	17,3	7,64	5,33	2,08
3	6,25	4,71	3,66	1,82
4	5,65	3,65	2,99	1,68
5	4,47	3,11	2,62	1,59
6	3,80	2,77	2,39	1,53
7	3,37	2,55	2,23	1,49
8	3,07	2,38	2,11	1,45
9	2,85	2,26	2,01	1,42
10	2,67	2,15	1,94	1,40
12	2,43	2,01	1,83	1,36
15	2,19	1,85	1,71	1,32
20	1,95	1,70	1,59	1,27
24	1,83	1,62	1,52	1,25
30	1,71	1,54	1,46	1,22
40	1,59	1,45	1,38	1,19
60	1,45	1,35	1,30	1,15
120	1,30	1,24	1,21	1,11

## 8.3 Requirements with respect to the RM

**8.3.1** For assessing measurement precision, an RM with sufficient homogeneity and stability is needed. The stability of the RM with respect to all properties of interest should at least be sufficient for the period of time that the precision checking measurements take. If necessary, specific precautions should be taken to monitor the stability of the RM used. Such precautions can consist of demonstrating the stability of the measurement process under study by other means, such as the use of a CRM, or by using another measurement process, the stability of which has been demonstrated.

**8.3.2** When using an RM for control charting, discrepant results can be caused by stability issues of the RM, rather than problems with the measurement system. Users of RMs should be aware of this possibility and include it in the root cause analysis.

**8.3.3** Although an RM used for assessing precision need not have metrologically traceable values for the properties of interest, precision can depend on the value of the measurand. Therefore, information about the nominal values of the properties of interest is usually required to assess the appropriateness of the RM selected for this application.

**8.3.4** More generic guidance on aspects to consider concerning the suitability of the RM can be found in [Clause 13](#).

## 8.4 Measurement

**8.4.1** The user should perform independent replicate measurements. “Independent”, in a practical sense, means that a replicate result is not influenced by previous measurements. To perform replicate measurements means to repeat the whole procedure. For example, in the chemical analyses of a solid material, the procedure should be repeated from the weighing of the test portion to the final reading or calculation of the result.

**EXAMPLE** If the measurement of lead in a soil RM consists of sub-sampling, destruction of the test portions, followed by measuring the aliquots, then the results are independent as far as sub-sampling, destruction and measurement are concerned. If, in contrast, one aliquot is measured repeatedly, then the standard deviation obtained only covers repeatability effects of measuring an aliquot.

Before starting experimental work, the user should check what part of the process is described by the standard deviation  $\sigma_{wo}$ . In many standards for testing, the repeatability stated refers to the whole standard test method. Consequently, the measurements for assessing the repeatability of such a test method should be carried out accordingly, i.e. repeating the test method for each and every (sub)sample completely.

**8.4.2** Independent replicate measurements can be achieved in various ways depending on the nature of the process. Parallel replication is not always recommended, however, because an error committed at any step of the procedure can affect all replicates. Furthermore, steps such as, for example, the calibration of the measurement equipment, can also be included in the replication process.

**EXAMPLE** In the case of iron ore analyses, replication of the analytical procedure is carried out at different times and includes appropriate calibration. In this case, the standard deviation calculated from the replicates also contains contributions from day-to-day variability and calibration.

## 8.5 Data treatment

**8.5.1** The data thus obtained should first be scrutinised for any irregularities. Data identified as technically invalid should be discarded, regardless of whether they seem to fit in the (assumed) probability distribution of the complete dataset. Technically invalid results are usually due to irregularities during either the sample processing or the measurement or both.

**8.5.2** A second type of irregularity includes observations whose values seem to be far away from the other observations in the dataset. Often, but not always, a technical explanation can be found and then these data should be discarded. If no technical explanation can be found, the data can be scrutinized for possible outliers using the methods described in ISO 5725-2 or ISO 16269-4. Outliers should be discarded or, in rare cases (e.g. calculation errors), replaced by corrected data. Whenever possible, outliers should be removed only on the basis of the outcome of more than one outlier test. As a rule, stragglers should be kept in the dataset.

The data treatment described can equally be applied to the other kinds of applications or purposes of an RM or a CRM (see also [6.1.1](#)).

**NOTE 1** An excessive number of suspected outliers indicates problems in the measurement process.

**NOTE 2** Removing outliers, stragglers in particular, reduces the scatter in the dataset and can consequently lead to a value of the standard deviation of the measurement process under study that is too small.

NOTE 3 The use of most outlier tests requires an assumption concerning the (expected) shape of the probability density function of the data. If such an assumption is inconsistent with the nature of the data, such an outlier test cannot be applied.

## 8.6 Calculation and assessment of precision

8.6.1 The precision of the measurement process is assessed by comparing the intralaboratory standard deviation under repeatability conditions with the specified value of the intralaboratory standard deviation,  $\sigma_{wo}$ .

Compute the average,  $\bar{x}$  (Formula (1)), and standard deviation,  $s_w$  (Formula (2)):

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (1)$$

$$s_w = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (2)$$

where

$x_i$  is the individual result;

$n$  is the number of results, excluding outliers.

8.6.2 Compute the following ratio (Formula (3)):

$$\chi_c^2 = \frac{s_w^2}{\sigma_{wo}^2} \quad (3)$$

where  $\sigma_{wo}$  is the specified value of the intralaboratory standard deviation.

Formula (4) denotes the 0,95<sup>th</sup> quantile of the  $\chi^2$  distribution with  $(n - 1)$  degrees of freedom, divided by the degrees of freedom  $(n - 1)$ .

$$\chi_{table}^2 = \frac{\chi_{(n-1);0,95}^2}{n-1} \quad (4)$$

Interpretation of  $\chi^2$ :

$\chi_c^2 \leq \chi_{table}^2$  There is no evidence that the measurement process is not as precise as required.

$\chi_c^2 > \chi_{table}^2$  There is evidence that the measurement process is not as precise as required.

NOTE Values for  $\chi^2$  can be taken from tables or computed by software. They can be found in many places, including Reference [22].

## 9 Bias assessment

### 9.1 General

9.1.1 Checking bias is a key application in laboratories. It can be performed as part of ensuring the quality of measurement results, method validation or both. For bias checking, it is essential that the reference against which the bias is checked is reliable, metrologically traceable and includes a statement of uncertainty.

**9.1.2** The CRM to be used for bias assessment is suitable if the type of material and the properties of interest are relevant for the intended use. The user should confirm the suitability of the CRM prior to the bias assessment. In particular, the uncertainty of the CRM should be sufficiently small to detect a significant bias.

**9.1.3** In this clause, guidance is given on bias assessment. Determining precision is dealt with in [Clause 8](#).

## 9.2 Approach to bias checking

**9.2.1** The use of a CRM for the purpose of bias checking contributes to the metrological underpinning of the measurement result. It is an essential activity in the validation of the measurement procedure.

**9.2.2** The observed difference between the measured value and the property value stated on the certificate should be smaller than the standard uncertainty associated with the difference, i.e. [Formula \(5\)](#).

$$|x_{\text{meas}} - x_{\text{CRM}}| \leq k \sqrt{u_{\text{meas}}^2 + u_{\text{CRM}}^2} \quad (5)$$

NOTE The choice of a coverage factor requires an (assumed) probability density function and a level of coverage. Often 95 % is used as the coverage level, but this choice can depend on the application.

**9.2.3** If the condition of [Formula \(5\)](#) holds, then the measured and property values are consistent with one another within their respective uncertainties. As the property value of the CRM is metrologically traceable to some stated reference, ideally the SI, the result obtained for the CRM confirms the metrological traceability of the results obtained from the measurement procedure.

**9.2.4** Users should calibrate their equipment independent of the CRM used for bias checking. The laboratory subsequently assesses the correctness of carrying out all steps in the measurement procedure by comparing the result with the stated property value. If the laboratory can use the same measurement procedure for its routine samples, it can demonstrate the metrological traceability of its result to the stated reference for the property value of the CRM.

NOTE 1 In practice, it can be necessary to modify some parts of the measurement procedure when applying it to the CRM. Modifications in the routine measurement procedure necessary for measuring the CRM can compromise the validity of the assessment. The more (or severe) modifications are necessary, the less useful the assessment becomes.

NOTE 2 In cases where the measurement procedure defines the measurand, e.g. enzyme measurements, changes in the measurement procedure will change the definition of the measurand.

**9.2.5** The evaluation of method bias as outlined in this clause is not limited to the use of a single CRM. If more than one CRM is available, it is recommended that more than one CRM is used to check the method over the range of values of the measurand relevant to the scope of the method.

## 9.3 Utilizing bias data

**9.3.1** Bias estimates obtained during bias assessment can sometimes be used to make corrections. However, the behaviour of the CRM(s) may not entirely reflect the behaviour of routine samples. In these cases, it is recommended that the method is improved so that the significance of the bias is eliminated, rather than attempting to correct for it. Some standard test methods give criteria for acceptable bias.

**9.3.2** The expression for bias is given by [Formula \(6\)](#):

$$d = x_{\text{meas}} - x_{\text{CRM}} \quad (6)$$

and its associated standard uncertainty is evaluated using [Formula \(7\)](#):

$$u(d) = \sqrt{u_{\text{meas}}^2 + u_{\text{CRM}}^2} \quad (7)$$

**9.3.3** If the bias is significant, i.e.  $|d| > U(d)$ , attempts are usually made to find the cause of the bias and to reduce or eliminate it.

NOTE  $U(d) = k \times u(d)$ , where  $k$  denotes a suitably chosen coverage factor.

**9.3.4** If sufficient reduction or complete elimination of the bias is not possible, the measurement result should be corrected for bias and the uncertainty associated with the bias should be included in the uncertainty evaluation. Corrections may be additive or multiplicative, depending on whether they depend on the value of the quantity to be corrected.

**9.3.5** If the observed bias is not corrected for and significant, it should be included in the uncertainty budget. A rough approximation is to add the square of the bias (i.e.  $d^2$ ) to the uncertainty budget to account for the uncorrected, significant bias.

**9.3.6** If the bias is evaluated over a range of values for the measurand, an average bias can be calculated, with its associated uncertainty. A general approach is given in ISO/IEC Guide 98-3:2008, F.2.4.5.

## 10 Calibration

### 10.1 General

**10.1.1** The use of a CRM for calibration of an apparatus is a convenient way to establish metrological traceability for the calibration function obtained with this apparatus. Usually the property value(s) of the CRM is used in the calibration model.

**10.1.2** A CRM shall be used for calibration. CRMs should be suitable for calibrating the equipment in terms of:

- a) physical form;
- b) appropriateness of the property (properties) certified;
- c) range of values and their relevance for the measurement range;
- d) appropriateness of its reflection of the behaviour of routine samples (commutability).

**10.1.3** It can be necessary to use a set of CRMs for instrument calibration, in particular if departure of proportional behaviour of the instrument reading with respect to the property value is possible.

**10.1.4** The uncertainty associated with the property value should be used in evaluating the uncertainty of measurement due to calibration. For this purpose, the law of propagation of uncertainty of ISO/IEC Guide 98-3 can be used, or any other mechanism for propagating probability distributions or uncertainties.

### 10.2 Practical considerations for calibration

**10.2.1** In some cases a relevant CRM is only available as pure substance, whereas the calibration method requires another physical form. If this is the case, the value as obtained during calibrant preparation and its associated uncertainty should be used in the measurement process.

**10.2.2** A quality control check should be applied when calibrating with CRMs. At a minimum, the calibration should be checked with, e.g., an independent RM or previously used material with a known value.

NOTE Checking the consistency of calibrations can be combined with other quality assurance measures assuring the validity of measurement results.

### 10.3 Calibration models

**10.3.1** CRMs shall be used for calibration when establishing metrological traceability and evaluating the uncertainty of measurement. The value assigned to the property of interest is entered in the calculation of the value assigned to the sample(s) measured. [Annex A](#) describes how the value of the CRM enters the calculations for four commonly used cases:

- single point calibration;
- bracketing;
- multipoint calibration;
- standard addition.

**10.3.2** Single point calibration is the simplest method; one calibrant (in this context the CRM) is used to calibrate the measurement equipment, which is then used to assign a value(s) to the sample(s) measured.

**10.3.3** Bracketing requires two calibrants, one with a property value greater than the value(s) of the sample(s) and one with a property value smaller than those values. By means of linear interpolation between the two calibrants, values are assigned to other samples.

**10.3.4** Multipoint calibration is widely used, in particular in analytical chemistry, to perform calibration of measurement equipment. A suite of calibrants is measured and, based on the responses measured, usually curvilinear regression is used to establish a relationship between the response measured and the quantity to be measured.

NOTE A simple form of a curvilinear relationship is a straight line.

**10.3.5** Standard addition means the calibration standard is added to the sample. The value of the measurand is determined by means of extrapolation.

**10.3.6** Expressions for assigning a value on the basis of these four mainstream approaches and the associated uncertainty evaluation are given in [Annex A](#).

## 11 Assigning values to other materials

### 11.1 General

**11.1.1** Particularly in instrument calibration, CRMs are often used to prepare other RMs by means of mixing, dilution or otherwise. The property value(s) for the newly prepared RM are partly based on the property value(s) of the CRM used for preparation. These applications are covered under the generic heading "assigning values to other materials". Methods of preparation include gravimetry and volumetry.

**11.1.2** Pure substance CRMs are often used for preparing mixtures or solutions which are in turn used for calibrating equipment. Sometimes, these mixtures or solutions are further diluted prior to use. The

concentration, amount-of-substance fraction or some other composition measure can be calculated on the basis of the purity data and the preparation data.

If the equipment used in the preparation process is calibrated appropriately and the environmental conditions are monitored accordingly, it is possible to obtain property values that are metrologically traceable to SI.

NOTE 1 Environmental conditions can play a dominant role in the accuracy of gravimetry. In particular when weighing voluminous objects, such as gas cylinders, air buoyancy can play an important role. The need for controlling environmental conditions depends on the rigour of the uncertainty evaluation and the desired level of accuracy.

NOTE 2 Concentration measurements are, among other things, temperature dependent. These effects can be small in view of other uncertainty components in a field laboratory, but they are not in view of other sources of uncertainty in the volumetric process.

**11.1.3** Checking the consistency of values assigned to these calibrants is recommended. Such checks can be performed:

- by comparing a new calibrant against an old, validated one;
- by assessing the effect of using the new calibrant as part of a quality control by, e.g., measuring a quality control material (QCM).

**11.1.4** Comparison of a new calibrant against an old, validated one is necessary if the calibration has a significant impact on the overall performance of the measurement procedure. The value calculated from the preparation of the new calibrant ( $x_{\text{prep}}$ ) should be compared with that using the old calibrant ( $x_{\text{meas}}$ ). The old, validated calibrant is used for calibrating the instrument used for the comparison. The new calibrant is validated if:

$$|x_{\text{prep}} - x_{\text{meas}}| \leq k \sqrt{u_{\text{prep}}^2 + u_{\text{meas}}^2}$$

where  $k$  denotes a suitably chosen coverage factor at a 95 % level of coverage. In most cases,  $k = 2$  is an appropriate choice (see ISO/IEC Guide 98-3:2008, Clause 7 for further guidance on choosing coverage factors).

Instead of applying the above criterion, the new calibrant can also be considered validated if the observed difference ( $x_{\text{prep}} - x_{\text{meas}}$ ) is small in comparison with the uncertainty required by the measurement or test method.

## 11.2 Pure substances

**11.2.1** Pure substances play a crucial role in establishing metrological traceability in many areas of measurement, in particular, but not limited to, chemistry.

NOTE “Pure” is an idealised concept, as is homogeneous or stable. In reality, no material is in an absolute sense pure.

**11.2.2** For composition measurements, pure substances often form the basis of what is called the “traceability chain”, i.e. it is the first link between the pure substance and composition measurements of the substance in question. Any material used for this purpose should have been characterized for impurities, and these should be identified and quantified as relevant for the intended use.

EXAMPLE 1 Nitrogen (6,0 grade) usually contains a few nmol mol<sup>-1</sup> benzene. This impurity is not relevant when making a synthetic natural gas mixture, where the amount-of-substance fraction of nitrogen is typically between 0,5 cmol mol<sup>-1</sup> and 20 cmol mol<sup>-1</sup>, and that of benzene, if at all, is in the range of 1 μmol mol<sup>-1</sup> to 10 μmol mol<sup>-1</sup>. However, it is highly relevant when making air quality standards (where the target amount fraction of benzene is 5 nmol mol<sup>-1</sup> to 50 nmol mol<sup>-1</sup>).

EXAMPLE 2 The presence of impurities in materials used for the fixed points on the temperature scale lead to deviations due to, e.g., freezing point depression.

**11.2.3** Many chemicals and other pure substances come with data concerning the impurities. This information is only useful in a metrological context if it specifies:

- units of measurement (e.g. mol/mol if expressed as amount-of-substance fractions);
- uncertainty associated with the assigned values.

**EXAMPLE 1** For a testing laboratory analysing trace contaminants in soil, it usually suffices to compare a calibrant prepared with the new pure chemical against an old calibrant, from which it has been established that it is not significantly biased. Such establishment can be obtained from, e.g., the repeated analysis of a QCM or proficiency testing material (PTM) or by using a CRM.

**11.2.4** Purity analysis is not limited to the pure substances being dissolved, diluted or otherwise made suitable for chemical composition measurement. The solvent, matrix gas, etc. should also undergo purity analysis, as it can also contain detectable quantities of impurities that can have an impact on the measurement results.

In measurement and testing, such purity analysis may be conducted as a reagent blank check, i.e. checking whether the level of impurities is sufficiently low to be neglected in subsequent steps in the measurement procedure.

## 11.3 Preparation of calibrants

**11.3.1** Gravimetry and volumetry are widely used as techniques for preparing calibrants.

The property values of calibrants are calculated based on the procedure used to prepare them. The uncertainty associated with the property values can be obtained using the law of propagation of uncertainty and the models indicated under [10.3.1](#).

**11.3.2** Many calibrants are not stable with respect to one or more properties over time. In order to obtain valid results during the calibration of an apparatus, the property values assigned earlier to the calibrant should still be valid within their respective uncertainties. It can be necessary to perform some kind of stability check. Stability checking of calibrants can be performed in many ways. Such methods include:

- a) conducting a stability test;
- b) comparing measurement results obtained using a new and old calibrant on the same sample, a retained PTM or a QCM;
- c) calibrating an instrument with the old calibrant and measuring the new one, followed by comparing the measured value against the value assigned to the calibrant;
- d) checking the entire measurement procedure with an independent CRM.

Stability testing can be laborious but can be necessary if there are no alternatives. Stability testing is covered in ISO 17034 and ISO 33405.

**11.3.3** The values assigned to calibrants should be valid for their entire lifetime. Laboratories should set such lifetimes to their calibrants to make specific checking unnecessary and rely on good quality control to detect issues with calibrants.

If such lifetimes are to be determined, the quality of the calibrant should be checked regularly so that metrological traceability of the results obtained with these calibrants is assured, in particular if they are used over longer periods of time.

## 12 Conventional scales

**12.1** Many measurement scales have been used since the earliest civilizations. Originally almost all of them were conventional, independent and inaccurate. Scientific and technical progress as well as international

trade have led to both the need for and the possibility of a unique, rational, self-consistent international system of units, the SI, which has been officially adopted worldwide. Nevertheless, it is not applicable to certain types of measurements for which it is necessary to create, sustain and use certain conventional units which are not within the scope of the SI. In other cases, the unit relating to the quantity to be measured lies within the frame of the SI, but the reproduction of the unit according to the definition is technically difficult and expensive. It is therefore more convenient to carry out the measurement on a practical scale of reference values assigned to material properties. Though a reference value scale and a pure conventional scale differ theoretically from each other, they are similar with respect to the use of RMs, and they will therefore be discussed together as conventional scales.

**12.2** Conventional scales are based on the values assigned to RMs. The assigned values are stated in standard specifications, international recommendations or other reference documents; therefore, an RM resulting in a fixed point on a conventional scale should have the same quality all over the world. CRMs of this type are certified for property values, i.e. they are measured on standard equipment with a reference measurement.

**12.3** It is evident that CRMs ensure only the fixed points of a measurement scale. Measurement on a scale requires either a fixed point and a mathematical function passing through it or two or more fixed points with stated means of interpolation between them.

NOTE Some special discontinuous scales exist, e.g. the Mohs scale for measuring hardness in geological tests. The scale is based on 10 minerals to which are assigned 10 grades of hardness; each harder mineral scratches a mineral at a lower grade of hardness.

**12.4** A conventional scale has two fundamental pillars: the CRM, providing the fixed point(s), and the standard specification (or similar document), giving the measurement procedure. Both should be strictly defined to ensure the compatibility of measurements on the conventional scale.

The standard specification provides detailed information necessary to establish and use a scale based on assigned values, or it may provide protocols for the experimental and calculation procedures to be used in measurements which depend on assumptions. It is advisable to specify the requirements of the CRM in the same standard specification as that in which the measurement procedure is described. By means of the necessary CRMs and relevant standard specifications, the user can create the measurement scale, and with the aid of such a scale can measure their sample or calibrate their instrument.

**12.5** To evaluate the uncertainty of a measurement on the scale, the user should consider the uncertainties in the creation of the scale and the uncertainty associated with the determination of its fixed points by the CRM. Sometimes the users demand a level of uncertainty in the end-use which is lower than the uncertainty of the fixed points defined by the CRM (e.g. in measurement of the pH of blood). The user should be aware that the uncertainty of the measurements on the scale is necessarily greater than the uncertainty of the fixed points. The replicated measurement of the CRM and the setting up of a scale (e.g. the appropriate selection of the points, the characteristics and repeatability of the interpolating instrument) also contribute to the overall uncertainty.

**12.6** The selection of CRMs for determining the fixed points of a scale should be directed by the required level of uncertainty of the end use. To minimize the uncertainty of the measured value on the scale, the user should employ CRMs which have been certified in terms of the units of the scale. The user is expected to be familiar with all relevant information about the measurement procedure for creating the scale and the instructions for the correct use of the CRM.

In certain cases, the user can apply pure chemical compounds for determining the fixed points, if CRMs certified in the scale units are unavailable or expensive or if their use is not necessary at the level of the uncertainty of the measurement. If this procedure is chosen, the user should be aware of the correlation between the purity of the material and the property on which the scale is based. The uncertainty of the measurement can only be evaluated roughly.

There is a wide variety of conventional scales and the methods of applying the CRMs to determine them differ widely. An example is given in [Annex C](#), for the conventional pH scale.

## 13 Selection of RMs and CRMs

### 13.1 General

**13.1.1** RMs, and CRMs in particular, can be used for various purposes in a measurement process. These purposes are listed in [6.1.1](#).

**13.1.2** It is recommended to use RMs and CRMs produced in accordance with ISO 17034. Evidence of such conformity should be available from the RM producer.

NOTE CRMs with long periods of validity that pre-date ISO 17034 accreditation can be considered acceptable if the issuer used processes that provide evidence of conformity to the precepts embodied in ISO 17034.

**13.1.3** Not every RM can be used for every purpose. Furthermore, a given RM can only be used for a single purpose in a specific measurement.

EXAMPLE A synthetic natural gas mixture certified for the contents of methane, ethane, propane, *iso*-butane, *n*-butane, nitrogen and carbon dioxide can be used for calibration of a gas chromatograph (GC). It cannot, in the same measurement, simultaneously be used to check the trueness of the GC. The same CRM can, however, be used to assess other aspects of performance, such as retention times, peak separation and precision.

**13.1.4** RMs can come in different forms.<sup>[21]</sup> Some of the common forms include:

- a) pure substances, characterized for chemical purity and other properties such as melting point, viscosity, enthalpy of combustion;
- b) standard solutions and gas mixtures, often prepared gravimetrically from pure substances;
- c) matrix RMs, characterized for the composition of selected properties, such as the content of specified chemical constituents; such materials may be prepared from naturally occurring materials or by synthesis;
- d) physical-chemical RMs, characterized for properties such as melting point, viscosity, octane number, flash point hardness and absorbance;
- e) reference objects or artefacts, characterized for functional properties such as taste or odour and including specimens characterized for properties ranging from fibre type to microbiological specimens.

Whether a CRM or some other kind of RM is selected for a particular purpose depends on many factors, including the specific application and the availability.

**13.1.5** RMs can be found in online databases such as COMAR,<sup>1)</sup> the key comparison database of the national metrology institutes, and the websites of RM producers and distributors.

### 13.2 Selection of a CRM

**13.2.1** For the purpose of this document, it is understood that any CRM is accompanied by an RM certificate as described in ISO 17034 and ISO 33401.

For CRMs intended for qualitative measurement, details can be found in ISO 33406.

**13.2.2** The intended use of a CRM states the purposes for which the CRM producer intends the material to be used in a measurement process.

**13.2.3** Laboratories should be able to explain and justify the basis of selection of all CRMs and any decision not to use a CRM. A formal suitability assessment should be performed by the user, unless it can be shown that

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1) <https://www.comar.org/>

the choice of RM will not significantly affect measurement results. The process of assessing the suitability of a CRM is shown in [Figure 2](#). The various aspects to be included in the assessment are given in [13.3](#).

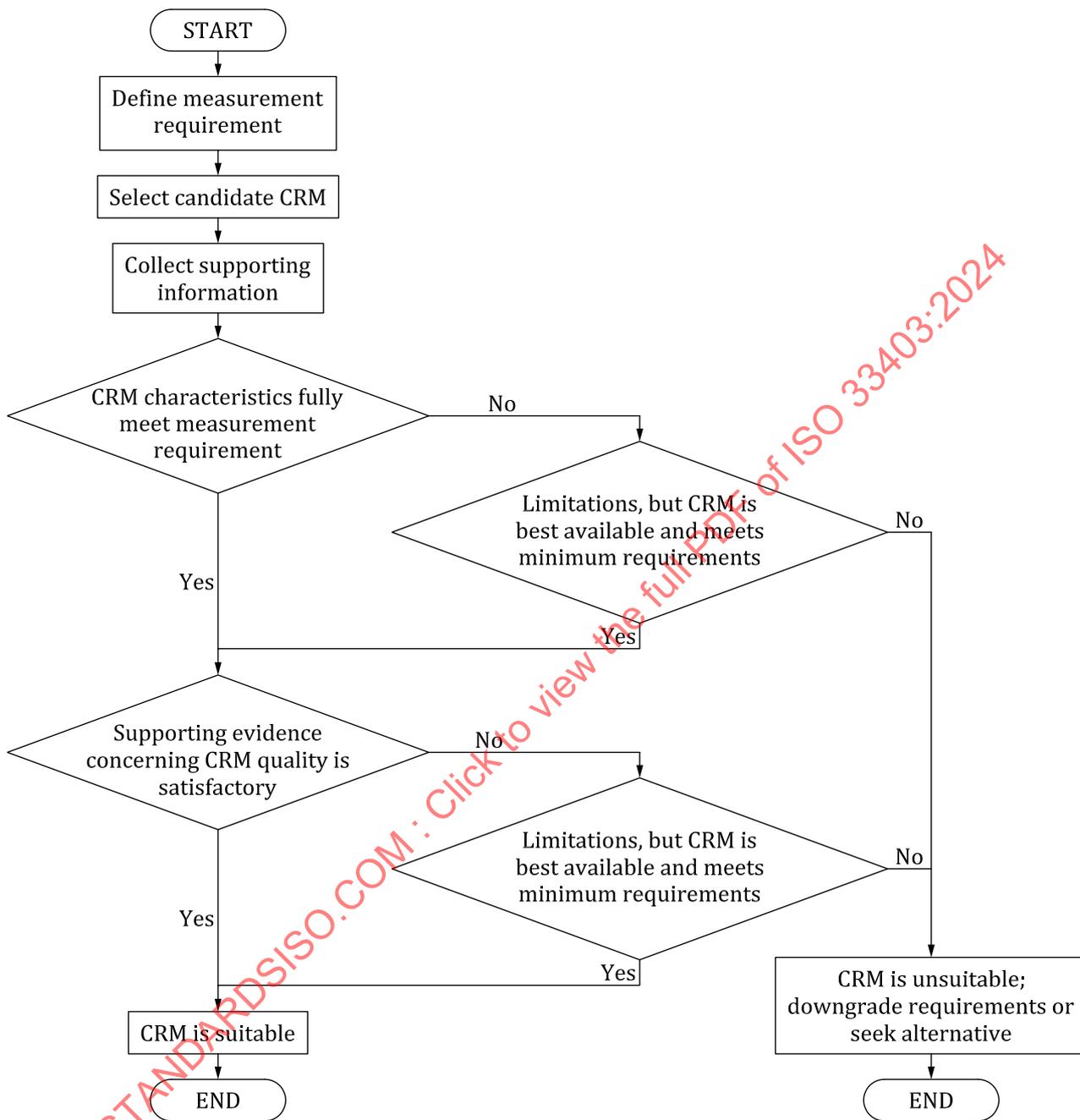


Figure 2 — Assessment of the suitability of a CRM

### 13.3 Selection of RMs

**13.3.1** RMs that come with stated property values should be produced in accordance with ISO 17034 and meet the requirements of ISO 33405 and therefore these property values should be metrologically traceable (preferably to SI). In order to fulfil their purpose, these RMs should come with a documentation package that contains at least the same information as would otherwise be stated on an RM certificate (see ISO 33401). For these RMs, the same considerations apply as for the selection of CRMs (see [13.2](#)).

**13.3.2** Many RMs come without stated property values. For most applications, the nominal values, or the range(s) within which the property value(s) are expected to fall, should be known. These RMs are often used for various kinds of precision control, such as day-to-day intralaboratory quality control. Furthermore, in order to be useful, these RMs should have been checked for homogeneity and stability as described in ISO 33405.

**NOTE** There are situations where RMs without, for example, stability data can still be usefully applied in measurement processes. These situations are limited to cases where the stability of the RM can be demonstrated indirectly by some other reference, such as including in the measurement process another RM (or CRM) from which the stability has been established.

### 13.4 Relevance to the measurement system

The user of the CRM should decide what properties of the CRM are relevant to the measurement procedure, taking into account the approach to certification, the statement on intended use and instructions for the correct use of the CRM on the certificate.

- a) **Level:** The CRM should have properties at the level(s) appropriate to the level at which the measurement process is intended to be used, e.g. concentration.
- b) **Matrix:** The CRM should have a matrix as close as possible to the matrix of the material to be subjected to the measurement process, e.g. carbon in low-alloy steel or carbon in stainless steel.
- c) **Form:** It may be a test piece or a manufactured article or a powder. It can need preparation. It should be used in the same form (e.g. solid, gas) as the sample to be measured.
- d) **Minimum sample intake:** Whenever the CRM certificate specifies a minimum amount that should be taken to obtain a sub-sample representative of the bulk, this specification should be adhered to.
- e) **Quantity:** The quantity of the CRM should be sufficient for the entire experimental programme, including some reserve if it is considered necessary. Avoid having to obtain additional new units of the CRM later in a given measuring process, unless the CRM is provided as single use units.
- f) **Stability:** Wherever possible the CRM should have stable properties throughout the experiment. Three situations can exist:
  - 1) The properties are stable and no precaution is necessary.
  - 2) The certified value of the properties can be influenced by storage conditions, in which case the container should be stored, both before and after its opening, in the way described on the certificate.
  - 3) The properties (which are changing at a known rate) at specific times are defined in a certificate supplied with the CRM. The user should obey the instructions for use as provided on the certificate or associated documents. The property values and stated uncertainties are only valid under these conditions.
- g) **Acceptable uncertainty of the certified value:** The uncertainty of the certified value should be compatible with the precision and trueness requirements.
- h) **Commutability:** Where relevant, the user should assess whether the CRM is commutable with respect to the intended use (see ISO 15194 and Reference [23]). Data from an assessment performed by the CRM producer can be available to aid assessing the commutability of the CRM by the user. In this case, matrix effects and effects due to sample preparation should be evaluated.

## Annex A (informative)

### Calibration models and associated uncertainty models

#### A.1 Single point calibration

**A.1.1** Given response  $y_{\text{CRM}}$  and  $y_{\text{sample}}$  obtained from measuring the CRM and sample respectively, and the property value  $x_{\text{CRM}}$  of the CRM, the result of the sample can be calculated using [Formula \(A.1\)](#):

$$x_{\text{sample}} = x_{\text{CRM}} \frac{y_{\text{sample}}}{y_{\text{CRM}}} \quad (\text{A.1})$$

The uncertainty associated with  $x_{\text{sample}}$  can be calculated from [Formula \(A.2\)](#):

$$u^2(x_{\text{sample}}) = x_{\text{sample}}^2 \left\{ \frac{u^2(x_{\text{CRM}})}{x_{\text{CRM}}^2} + \frac{u^2(y_{\text{CRM}})}{y_{\text{CRM}}^2} + \frac{u^2(y_{\text{sample}})}{y_{\text{sample}}^2} \right\} \quad (\text{A.2})$$

The uncertainty  $u(x_{\text{sample}})$  covers only effects from repeatability of measurement and the uncertainty associated with the property value of the CRM; this uncertainty budget should usually be complemented with uncertainty contributions from, for example, sampling, sub-sampling and sample transformation.

**A.1.2** The use of this model and associated uncertainty evaluation is limited to situations where the relationship between the  $x$  and  $y$  variables can be modelled accurately over the range of interest using the relationship:

$$y = a_1 x$$

where  $a_1$  denotes the slope. If there is a significant zero deviation or there is nonlinearity to be considered, the single-point calibration model can be invalid or other terms should be included in the expression for the standard uncertainty.

#### A.2 Bracketing

**A.2.1** Bracketing requires two CRMs, one in value above the value of the unknown sample and one below this value. The results of the two CRMs are used for linear interpolation. Hence, the interval chosen should be small enough so that non-linearity of the detector (if any) does not lead to a bias in the value assigned to the unknown sample. Consequently, the maximum size of the interval depends on the non-linearity of the measurement system used.

**A.2.2** The model for bracketing reads as in [Formula \(A.3\)](#):

$$x_{\text{sample}} = \frac{x_2 - x_1}{y_2 - y_1} (y_{\text{sample}} - y_1) + x_1 \quad (\text{A.3})$$