Designation: E3330 – 22

Standard Guide for Contents of Documentation and Statistical Treatments for Reference Materials for Metals, Ores, and Related Materials[1]

This standard is issued under the fixed designation E3330; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide is designed to explain and to clarify documentation that accompanies an RM or a certified reference material (CRM). It explains the contents of certificates of analysis for CRMs and product information documents for RMs, based on existing international standards and guides. It briefly touches on the minimum requirements for a label attached to the CRM/RM unit or unit container and to the package containing the unit or unit container.

1.2 This guide provides some basic guidance on calculation of consensus values and uncertainty estimates for CRMs and RMs with examples of approaches commonly used by national metrology institutes and suggestions for sources of information.

1.3 *Units*—The values stated in SI units are to be regarded as the standard, whenever applicable. Values can be traceable to other higher-order reference systems, including Rockwell Hardness, pH, and other systems defined by an international standard or peer-reviewed publication.

1.4 *Contents*—Sections and topics within this guide are enumerated below:

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E18 Test Methods for Rockwell Hardness of Metallic Materials

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E382 Test Method for Determination of Crushing Strength of Iron Ore Pellets and Direct-Reduced Iron

E1447 Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by Inert Gas Fusion Thermal Conductivity/Infrared Detection Method

E2972 Guide for Production, Testing, and Value Assignment of In-House Reference Materials for Metals, Ores, and Other Related Materials

2.2 *ISO/ANSI Standards:*[3]

ANSI/NCSL Z540-2-1997 (R2012) American National Standard for Expressing Uncertainty – U.S. Guide to the Expression of Uncertainty in Measurement

ISO Guide 30:2015 Reference Materials – Selected Terms and Definitions

ISO Guide 31:2015(E) Reference Materials – Contents of Certificates, Labels and Accompanying Documentation

[1] This guide is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.22 on Laboratory Quality.

Current edition approved April 1, 2022. Published April 2022. DOI: 10.1520/E3330-22.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

ISO Guide 33:2015 Reference Materials – Good Practice in Using Reference Materials

ISO Guide 35:2017 Reference Materials – Guidance for Characterization and Assessment of Homogeneity and Stability

ISO Standard 17034:2016(E) General Requirements for the Competence of Reference Material Producers

2.3 *BIPM Standards:*[4]

JCGM 100:2008 Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement (GUM 1995 with Minor Corrections)

JCGM 101:2008 Evaluation of Measurement Data – Supplement 1 to the "Guide to the Expression of Uncertainty in Measurement" - Propagation of Distributions Using a Monte Carlo Method

JCGM 200:2012 International Vocabulary of Metrology – Basic and General Concepts and Associated Terms; (VIM), 3rd Edition, 2008 Version with Minor Corrections.

3. Terminology

3.1 *Definitions*—For the purposes of this guide, the terms and definitions given in ISO Guide 30, ISO Guide 31, and ISO Guide 35 are normative. Definitions in JCGM 200:2012 are informative.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *censored data, n*—censoring of data is a condition in which the value of a measurement result is only partially known, because the value either (*1*) is less than a limit of quantification or detection, (*2*) exceeds the upper limit of observation of the instrument, (*3*) has been rounded severely by the analyst, or (*4*) has been intentionally reported as falling within one of a set of predefined intervals.

3.2.1.1 *Discussion*—Case (1) refers to results that are not quantitative and may be reported as less than either the limit of quantification or the limit of detection. Case (2) is exemplified by using a balance with a capacity of 200 g to weigh a mass of 210 g. The result would be reported as > 200 g. More common in analytical chemistry is case (3), the act of censoring in which the laboratory deliberately rounds the result to an extreme in an effort to be conservative with clients. For example, a test method may be able to give quantitative results to 0.001 %, but the lab routinely reports values rounded to 0.01 %. This causes all values between 0.005 % and 0.014 % to be given the same value of 0.01 %. The true variance of the measured property is obscured. Case (4) is nearly the same as case (3), except the method of reporting is predefined as placing results into a set of categories, such as 1 to 10, 10 to 20, 20 to 30, etc. The problem of censored data, in which the observed value of some variable is partially known, is related to the problem of missing data, where the observed value of some variable is unknown. Censoring should not be confused with the related idea of truncation. With censoring, observations result either in knowing the exact value that applies, or in knowing that the value lies within an interval. With truncation, observations never result in values outside a given range. Values outside the range are never seen or never recorded. Truncation is not the same as rounding (Appendix X3, X3.3). Types of censoring important to RM development include the following:

Left censoring—a result is below a certain value, but it is unknown by how much.

Right censoring—a result is above a certain value, but it is unknown by how much.

Interval censoring—a result is somewhere in an interval between two values, which includes both a set of intervals predefined prior to measurement and cases of rounding after measurement.

3.2.2 *non-operationally defined measurand, n*—measurand defined independently of any specific measurement procedure.

3.2.3 *operationally defined measurand, n*—measurand that is defined by reference to a documented and widely accepted measurement procedure to which only results obtained by the same procedure can be compared. (See ISO 17034:2016(E), p 3.)

4. Summary of Guide

4.1 This guide discusses steps for implementing a procedure to document and label RMs and CRMs. Specifications for RM product information sheets, CRM certificates of analysis and labels for unit containers discussed in this guide include those mentioned in technical clauses of ISO Guide 30, Guide 31, and Guide 33.

4.2 This guide includes guidance and suggestions for processes for critical evaluation of data created in development of RMs and in calculations of consensus values and uncertainty estimates and their presentation in certificates of analysis for CRMs and product information documents for RMs.

5. Significance and Use

5.1 This guide is intended for use by developers of RMs and CRMs for the metals and mining industries.

5.2 The guidance is related to uniform procedures and requirements and is intended to prevent the proliferation of widely varying documentation practices, definitions, and terminology. Where the statements in this guide are made as imperatives, it is because the stated practices are fundamental to chemical metrology, not to CRM/RM development.

5.3 The material in this guide is intended to supplement and to clarify the contents of ISO Guide 31 and to provide guidance specific to the needs of the metals and mining industries.

5.4 The documents described in this guide are intended to contain the minimum amount of information required for a user to understand the material, to help a user judge the quality of the product, and to help a user employ it in appropriate ways. Neither this guide nor resultant documents are meant to be encyclopedic.

5.5 Because this document is a standard guide, it is intended to educate those who are involved in laboratory operation, quality system development and maintenance, reference material development, and accreditation of laboratory operations within the scope of a quality system. It must be understood by all parties that the elements of this guide discuss optional

[4] Available from International Bureau of Weights and Measures (BIPM), https://www.bipm.org.

practices having numerous choices for accomplishment and documentation. However, this guide does not constitute requirements for assessment and accreditation. An obvious example is statistical evaluation for consensus value and uncertainty calculations, which can take many forms with no single, correct choice for any given case.

5.6 When using this guide, CRM developers will set goals for the material under development, such as target uncertainties for homogeneity and for overall coverage intervals for assigned values. These choices are based on the intended uses of a CRM. The material, property values, and their uncertainties may or may not meet the set goals. These decisions are made using expert judgement, and there are no exact right or wrong, passing or failing outcomes that should be imposed by outside authorities. The quality of a CRM or RM will be judged by the prospective user, who needs it to use with their measurement process.

5.6.1 An example of a requirement a CRM user may have is whether the uncertainty of a certified value is fit for the purpose of using the value as a calibration point. CRM users and producers can obtain information from standard test methods or from laboratories doing relevant analyses.

5.6.2 Although the ISO Committee on Reference Materials (ISO TC334) has designated all CRMs and other forms of RMs as being named reference materials, this guide uses the convention the certified reference materials are called CRMs and reference materials having no certified values are named RMs. This practice is consistent with Guide E2972.

6. Contents of a Certificate of Analysis or Reference Material Documentation

6.1 This section concerns information contained in each type of RM document. A summary of the requirements is given in Table 1 in which the categories of information are designated in the ISO 17034 system (see ISO Guide 31:2015) as mandatory, recommended, and optional for both CRM and RM documents. The category titles are discussed in the preferred order of presentation with the preferred terminology, and it is recommended to retain the preferred order and listed titles to benefit users by increasing standardization among RM producers. However, the order and titles of the categories may be adjusted to suit the preference of the RM producer. The information is presented as required for a CRM certificate of analysis. Product information sheets for RMs require less information in some categories and more information in others.

6.2 *Categories of Information in CRM and RM Documents*

6.2.1 *Title of Document*—Provide a distinct title.

6.2.1.1 For CRMs, the preferred title is ‘Certificate of Analysis’.

6.2.1.2 For RMs, the preferred title is ‘Product Information Sheet’. Avoid the use of the word certificate, or its derivatives, because RMs do not have certified values. Some RM producers have used the terms ‘report of analysis’ and ‘material information sheet’.

6.3 *Unique CRM/RM Identifier*—A unique combination of a product code and a batch number is one example of a unique identifier by which a new CRM is distinguishable from the material and document of any other CRM/RM.

6.4 *Name of CRM/RM*—As far as possible, the name should describe the material in enough detail to distinguish it from similar materials. Thus, the name of a rock or ore followed by its origin or a compositional characteristic gives more individuality to geological materials. For metallurgical samples, it is appropriate to indicate the composition of the important elements, for example, “6Al-4V Titanium Alloy”, or to use an

TABLE 1 Contents of a Certificate of Analysis or a RM Document

Content	CRM Certificate of Analysis	RM Document	Subsection
Title of Document	Mandatory	Mandatory	6.2
Unique CRM/RM Identifier	Mandatory	Mandatory	6.3
Name of CRM/RM	Mandatory	Mandatory	6.4
Description of Material	Mandatory	Recommended	6.5
Intended Uses	Mandatory	Mandatory	6.6
Property, Property Value, and Associated Uncertainty	Mandatory	Optional	6.7
Metrological Traceability	Mandatory	Optional	6.8
Methods for Non-Operationally Defined Measurands	Recommended	Recommended	6.9
Methods for Operationally-Defined Measurands	Mandatory when applicable	Recommended	6.10
Minimum Recommended Sample Quantity	Mandatory when applicable	Mandatory when applicable	6.11
Homogeneity	Mandatory	Mandatory	6.12
Period of Validity	Mandatory	Mandatory	6.13
Name and Contact Details of Producer	Mandatory	Mandatory	6.14
Name and Function of Approving Officer	Mandatory	Optional	6.15
Non-Certified Values	Optional	Optional	6.16
Storage Instructions	Mandatory	Mandatory	6.17
Handling and Use Instructions	Mandatory	Mandatory	6.18
Collaborators	Optional	Optional	6.19
Sub-Contractors	Optional	Optional	6.20
Reference to Certification Report	Optional	Optional	6.21
Referenced Documents	Recommended	Optional	6.22
Page Number and Total Pages	Mandatory	Mandatory	6.23
Document Version	Mandatory	Mandatory	6.24
Commutability	Not Applicable	Not Applicable	6.25
Health and Safety Information	Optional	Optional	6.26
Legal Notice	Optional	Optional	6.27

industry standard alloy identification code, for example, from the Unified Numbering System. If several similar CRMs are available, the nominal level(s) of key constituent(s) can be included, for example, SRM 2453a Hydrogen in Titanium Alloy (Nominal Mass Fraction 125 mg/kg H). In cases where two or more physical forms of a material are offered, it may help to include the form in the name, for example, SRM 1264a High-Carbon Steel (Modified) (disk form).

6.5 *Description of Material*—A brief description of the material should be given in a certificate of analysis to provide a more detailed explanation of the name. For materials certified for their chemical composition, the main characteristics of the matrix may be of importance in applications to analytical methods.

6.5.1 The physical description of the material should be given, where appropriate, for example, particle size range, as-supplied dimensions of metal cylinders, rods, pins or disks, and the nature of the container in which it is supplied, if applicable.

6.5.1.1 In cases of items consumed during use, the dimensions, quantity, mass, etc. would be listed for a sales or distribution unit.

6.5.2 Additional, optional details on the matrix composition may be important. Consider including the information on the following, if appropriate:

6.5.2.1 Alloys custom-made to a modified alloy specification;

6.5.2.2 Whether analytes were spiked in or are naturally present;

6.5.2.3 The presence or absence of interfering substances, even if not quantified.

6.6 *Intended Use(s)*—Potential users need to know the intended uses of a CRM/RM. When the provided properties are independent of measurement procedure, this statement is not intended to restrict the use for other purposes. The CRM/RM document should provide enough information for the user to decide whether the material meets their requirements (for example, matrix type, measurand, quantity level, uncertainty estimate, etc.). Because there may be uses for which the material is not appropriate or has not been characterized, the document may include a statement explaining restrictions.

6.6.1 Examples of intended uses for a CRM include the following:

6.6.1.1 Confirm the degree of equivalence of measurement results from multiple laboratories, or promote harmonization, if necessary;

6.6.1.2 Transfer of property values among different materials;

6.6.1.3 Validation of analytical methods, especially regarding trueness;

6.6.1.4 Calibration of instruments or measurement processes;

6.6.1.5 Determination of the recovery factor of a matrix separation operation;

6.6.1.6 Realization of a fixed point of a (international) measurement scale.

6.6.2 Examples of intended uses of an RM (other than a CRM) include the following (Note 1):

6.6.2.1 Demonstrate control of a measurement process in a laboratory over time, also known as statistical process control;

6.6.2.2 Check instrument operational performance, including sensitivity and repeatability;

6.6.2.3 Conduct reproducibility studies, that is, repeated use over an extended time, multiple instruments, multiple analysts, etc.;

6.6.2.4 Confirm the degree of equivalence of measurement results from multiple laboratories, or promote harmonization, if necessary;

6.6.2.5 Investigate impacts of changes to environmental conditions (for example, temperature, humidity).

6.6.2.6 More information on RMs, in particular in-house RMs, can be obtained from Guide E2972.

NOTE 1—While it is true that CRMs can be used for these same functions as RMs, it is generally discouraged, because CRMs are typically harder to develop, more expensive, and rare. RMs suitable for these purposes can be developed without having to implement an accredited quality system and with far less analytical effort.

6.7 *Property, Property Value, and Associated Uncertainty*—A CRM certificate should contain a clear statement of each constituent and property of interest, its assigned value and associated uncertainty (Note 2). A RM document most often will contain a statement of each constituent or property, along with its assigned value. The RM document may or may not include an associated uncertainty for each value. In some cases, a RM may not have an assigned value, when its purpose is research into one or more measurement processes. See also 10.2.

6.7.1 This document makes no distinction between quantitative and nominal properties, nor between measurement and examination.

6.7.2 Each constituent or property should be described as its measurand. Consider including a clear statement defining the identity of each item measured and the matrix in which it is found. When the measurand is defined by a standard that describes a system of units other than the SI or by a standard method that defines the constituent or property, the definition will include the operation(s) necessary to realize the definition. See ISO Guide 35 for a brief discussion of measurands that are operationally-defined by a standard.

6.7.2.1 For example, a non-operationally defined measurand for iron in a nickel alloy could be described as follows: *The measurand is the total amount of the element iron in a nickel matrix.*

6.7.2.2 Another example of a non-operationally defined measurand is hydrogen in titanium, which can be described as follows: *The measurand is the total amount of hydrogen in a titanium matrix as realized using the inert gas fusion test method in ASTM E1447 – 09(2016), calibrated using the certified value for total H in NIST SRM 2453a Hydrogen in Titanium Alloy (Nominal Mass Fraction 125 mg/kg H).* Test Method E1447 has been validated as providing the total hydrogen content of Ti alloys (when properly implemented). The statement of calibration using the NIST (National Institute of Standards and Technology) SRM confirms that the identity of the measurand is non-operationally defined, because this

SRM was value assigned using both inert gas fusion and prompt gamma-ray activation analysis – two independent test methods.

6.7.2.3 Possibly the best-known example of an operationally-defined measurand in the metals industry is the Rockwell C Hardness scale as defined in Test Methods E18.

6.7.2.4 An example of an operationally-defined measurand in the mining industry is Test Method E382. The measurand definition is stated as "*crushing strength*, n—average compressive load needed to break the pellets in the test sample completely." The load is force expressed in the SI unit of kilogram, which is not a force unit. However, the standard method includes numerous operational requirements, including a narrow range of iron ore pellet diameters to be agreed by the parties concerned, the requirement for a constant rate of force application, the requirement for the analyst to judge when the pellet is broken, and no evaluations of precision and bias for the method. In addition, there is a note warning that results may differ depending on the test machine used and the speed of platen motion during force application, which is controlled within ± 32 % relative to the nominal speed.

NOTE 2—The term constituent is included in this discussion because it refers to a component, typically a chemical component, that is part of the composition of a material. While the amount of a constituent is technically a property of a material, the distinction is useful for chemical metrology in which instrumental test methods are used to identify the presence of a chemical constituent and to quantify the amount present. In the metals and mining industries, it is common for product testing activities to be differentiated between chemical and physical properties.

6.7.3 Certified values are required by ISO Guide 31 to be clearly indicated as certified values. It is recommended practice to also keep certified and non-certified values separate within a certificate, when both types of values are provided.

6.7.4 An associated uncertainty estimate must be provided for all assigned certified values. For the highest confidence in estimates of the true value, it is better for the uncertainty to be an overall uncertainty that contains contributions from all important sources in the results used to calculate the assigned value. The associated uncertainty of each value should be reported according to the Guide to the Expression of Uncertainty in Measurement (JCGM 100:2008) and its Supplement 1 (JCGM 101:2008). See Section 10 for in-depth discussion.

6.7.4.1 All uncertainty estimates must be accompanied by a definition of the estimate. The definition should give the name of the uncertainty, *viz.* standard deviation, combined standard uncertainty, coverage interval, expanded uncertainty (Note 3), etc. If it is a coverage interval, that means the level of confidence and either the degrees of freedom, the coverage factor, or both. It is advisable, but optional, to make a brief statement of the components of uncertainty included in the stated uncertainty value. See Section 10 for discussion of uncertainty components.

6.7.4.2 The provision of a numerical uncertainty estimate with a non-certified value is optional.

6.7.4.3 For nominal properties and for non-certified values for which no numerical uncertainty estimate is provided, the uncertainty estimate should take the form of a statement describing the level of confidence the issuing body has in the nominal or numerical value.

(1) An example can be taken from positive material identification of alloys using a portable spectrometric technique. In such methods, the spectrum of a sample of scrap may be compared to a library of spectra to identify the family of alloys or the specific alloy of the sample. The statement of uncertainty can be as simple as *the level of confidence is very high that the measured alloy is a type of Ni-Co alloy*. This is a qualitative statement without numerical attributes. See 11.2.

6.7.4.4 More than one type of uncertainty may be provided in the same document. A certified value should always have an associated overall coverage interval. In addition, it may be important to provide an estimate of the standard deviation of individual measurements for a material that will be used as a calibration standard. An RM intended for process control measurements can be expected to be more useful if it has an estimate of the repeatability standard deviation from a properly functioning instrument. There are test methods that require multiple measurements to exhibit repeatability better than a minimum requirement.

NOTE 3—The terms coverage interval and expanded uncertainty are interchangeable for practical purposes. Both provide a means to show a range within which the assigned value is believed to be.

6.7.5 It is important to briefly discuss the concept of *true value* as it applies to certified and non-certified values. At the highest level of chemical metrology, a *true value* is the perfectly known number for the amount of substance or physical characteristic being measured.

6.7.5.1 It is impossible to know a *true value* with complete certainty, because that requires perfection in all aspects of the measurement process and a perfect realization of the definition of the measurand. During reference material development, the project staff will decide whether their processes are capable of providing a consensus result that together with its uncertainty interval is believed to include the true value with a high degree of confidence. The key to making this decision is deciding if the value assignment process includes all conceivable sources of uncertainty and if all applied test methods for each constituent or property provide the same definition of the measurand, perhaps with a component of uncertainty relating to the definition.

6.7.5.2 The alternative concept is that the value to be assigned and its uncertainty interval cannot be claimed to include the true value. This situation could arise when a development project does not include sufficient information about the different possible ways of realizing a measurement of the defined amount of substance or property value. For example, the developing organization may have performed measurements using only their implementation of a standard test method. They may have performed measurements using several different analysts, each working with a different brand of instrument. However, they may know that there are other choices of equipment, measurement conditions, reagents, etc. that have not been tested. In this case, the developers may decide to state that their assigned value and its uncertainty cover only the range of results expected with the material and the test method employed, even when they believe metrological traceability to a higher-order reference system has been

established. They may even decide to state that their assigned value is for an operationally-defined measurand.

6.8 *Metrological Traceability*—This is a difficult concept, requiring careful consideration of calibration standards, whether uncertainty estimates include all necessary components of uncertainty, and how the measurand is defined. According to international standards and guides on certification, the information on metrological traceability that shall be stated in a CRM certificate of analysis is the higher order reference system, units or scale, to which the property value is made traceable. Multiple measurands may be covered by a single statement or multiple statements, as appropriate.

6.8.1 For example, the traceability statement to be made with the measurand defined in 6.7.2.1 could be as follows: *The certified value is traceable to the derived SI unit of mass fraction expressed as percent (%).*

6.8.2 For example, the traceability statement to be made with the measurand defined in 6.7.2.2 could be as follows: *The certified value is traceable to the derived SI unit of mass fraction expressed as milligrams per kilogram (mg/kg).*

6.8.3 The concept of metrological traceability covers the relationship between values and their units of measurement. Values with units and uncertainty estimates are traceable to other values with units and uncertainty estimates through calibration of the measurement process(es) and definition of the measurement scale.

6.8.4 Some CRM producers make incorrect statements of traceability by referring only to the CRMs used in the project. This is an oversimplification that leads to misunderstanding of the concept of traceability. A list of CRMs used in a certification project does not constitute a statement of metrological traceability. It is not correct to state that a value is traceable to a CRM or its producer or other organization, because values are traceable to other values or to a measurement process that defines a reference scale. See Note 4.

6.8.4.1 It is not necessary to use a CRM to establish metrological traceability to a system of measurement units. A laboratory can establish traceability by calibrating their test method using a pure compound or pure element. The compound or element must have an assay with a stated uncertainty, either from the provider or developed by the user. There are papers on the topic in the scientific literature, for example those by Gotthard Staats on the realization of trueness (for example, Ref (**1**).)[5]

6.8.4.2 A laboratory using a classical test method, such as a gravimetric, coulometric or volumetric method, can establish traceability by using standardized reagents, calibrated balances, calibrated power supplies, and calibrated glassware.

NOTE 4—A reference material producer (RMP) may provide a list of CRMs used in a certification project for the purpose of providing additional assurance to the user that appropriate materials were employed. However, such a list does not serve as the statement of traceability.

6.8.5 A value can be traceable to a measurement process that defines the scale of units for the measurand. One example is pH, where the Harned cell construction and its use with the Bates-Guggenheim Convention define the pH scale. Another example is the Rockwell C Hardness scale as defined in Test Methods E18.

6.8.6 It is not necessary for all test methods used for a given measurand to be capable of establishing metrological traceability to the highest order reference system. That is ideal, but it only takes one link.

6.9 *Methods for Non-operationally Defined Measurands*—When the measurand is not defined by the measurement process(es), it is not necessary to include the measurement processes in the documentation. However, the RMP may choose to do so by listing the measurement method(s)/technique(s) of characterization, the approach for characterization (for example, single method, multiple methods, etc.), and if applicable, the method(s) used for sample preparation for measurement.

6.9.1 The two most recognizable means of establishing non-operationally defined measurands are (*1*) use of a measurement process independently confirmed as having minimal bias with all sources of uncertainty taken into account, and (*2*) use of multiple, independent measurement processes, where the results from the multiple processes demonstrate a high enough level of equivalence and all sources of uncertainty are taken into account. In other words, any detected bias between the results is low enough that the overall uncertainty of a consensus value is fit for the intended purpose(s) of the CRM. The phrase 'taken into account' does not mean one must estimate every uncertainty component no matter how small. It means the developer will ensure that nothing substantial was overlooked.

6.9.2 In a case where no bias is detected, the bias detection limit must be low enough to be fit for purpose. For guidance on estimation of bias detection limit, see ISO Guide 33.

6.10 *Methods for Operationally-Defined Measurands*—When the definition of a measurand depends on the measurement method, the certificate or report document should explain, for example, by describing the method or giving a reference to a publication in which the method is described. The same principle applies in the case of nominal properties.

6.11 *Minimum Recommended Sample Quantity*—Whenever applicable, the minimum recommended sample quantity of the material should be based on heterogeneity or on other considerations such as stability or a defined measurement process. This should be accompanied by a statement that the property value and its associated uncertainty are only guaranteed if minimum sample quantity is respected. See the related discussion of heterogeneity in 6.12. Examples of this quantity include the following:

6.11.1 A minimum mass used with one or more measurement processes that exhibited repeatability fit for purpose;

6.11.2 A minimum area of measurement or a minimum number of independent, measured locations by, for example, X-ray fluorescence spectrometry and spark or laser ablation spectrometry methods, respectively.

6.11.3 The CRM/RM document may specify a procedure to ensure a representative subsample is used. See Note 5.

NOTE 5—It may be appropriate and important to communicate to the

[5] The boldface numbers in parentheses refer to a list of references at the end of this standard.

user that, in cases where the test method cannot measure in a single measurement a quantity of material greater than or equal to the minimum recommended quantity, multiple measurements of smaller quantities, that together equal or exceed the minimum recommended amount with calculation of the mean result from the multiple measurements, may meet the user's need and still be consistent with the assigned value and its uncertainty estimate.

6.12 *Heterogeneity*—An assessment is required to establish the degree of heterogeneity of the material with respect to the property of interest and to ensure it is fit for the intended purpose(s) of the material. It is recommended the description be brief, especially if the heterogeneity is found to be very low. The developer of the material may wish to consider listing the test method(s) used for characterization.

6.12.1 An estimate of variance arising from compositional heterogeneity is a necessary component of uncertainty.

6.12.1.1 Heterogeneity assessment includes variance within an individual unit of the material and variance among units. The overall question is whether a user can expect to obtain the same test result from two or more samples taken from a single packaged unit as well as two or more samples taken from different units.

6.12.1.2 If material composition variance is high in comparison to the repeatability capability of one or more measurement processes within the scope of intended uses of a material, it is necessary to include heterogeneity variance in the overall uncertainty analysis (the uncertainty budget) for the value of a constituent.

6.12.1.3 If variance is low in comparison to the repeatability capabilities of all measurement processes in the scope of intended uses, a statement of that fact is enough, and an explicit statement of an estimate of heterogeneity variance is not necessary.

6.12.2 Analysis of variance (ANOVA) is a powerful tool for the study of sources of variance in data sets. It is frequently applied to the study of heterogeneity within and among packaged units of reference materials. It often has practical limits. For example, in a case when the repeatability standard deviation of all individual measurements is much less than the standard deviation required for the material to be fit for purpose and the tested sample quantity is less than the smallest amount required for testing, the material is automatically deemed acceptable. It matters not what the ANOVA statistics show.

6.13 *Period of Validity*—A period of validity may take the form of an expiration date or a statement of indefinite validity. The fitness for purpose of the material cannot be guaranteed beyond the stated period.

6.13.1 The issuing organization is expected to monitor the material during its period of validity and to notify users of substantive changes in a timely manner. It is recommended to include a statement of this commitment.

6.13.2 It is not recommended to state the period of validity as a function of the time since purchase.

6.13.3 It is appropriate to provide instructions for a material that begins to change when the unit container is opened. Some materials may require packaging in single-use containers.

6.13.4 It is recommended to include a statement that some circumstances will invalidate the certification, such as damage, contamination, improper storage, failure to follow instructions for sampling, handling, and storage, or other serious issues.

6.13.5 If the material or its intended use is such that periodic recalibration or recertification is necessary, it is appropriate to include an explanatory statement. When appropriate, some CRM producers find it helpful to state that no recalibration or recertification is needed to forestall questions and unnecessary work by the users.

6.13.6 For cases in which a material is such that each piece may be measured repeatedly by the user, it may be necessary for the producer to address the effects of repeated measurement on the stability or other aspects of utility of the piece of material. This is not technically an issue of period of validity of a CRM or RM. Rather, it is something that should be handled through instructions for handling and use. See 6.18.2.

6.13.7 When circumstances require that a CRM certificate or RM document be revised, the issuing RMP should include a history of changes in the revised document.

6.14 *Name and Contact Details of the Producer*—The name and contact details of the CRM/RM producer may include postal address, telephone number, fax number, e-mail address, and website.

6.15 *Name and Function of Approving Officer*—State the name(s) and function(s) of an officer(s) representing the producer and accepting responsibility for the contents of the certificate of analysis.

6.16 *Non-Certified Values*—The CRM/RM producer may include non-certified values.

6.16.1 Examples of non-certified values include the following:

6.16.1.1 The approximate mass fraction of an analyte in a complex matrix that does not fulfill the criteria established by the issuing RMP for a certified property value;

6.16.1.2 Individual results from each laboratory or analyst, where results from several laboratories or analysts were used to assign the property value(s).

(1) Publishing individual results from collaborating laboratories is allowed, but it should be done with great care. The data may create confusion or reduce the trustworthiness of the CRM, especially where some value(s) may be construed as discrepant. The data may also be misused by analysts, who prefer one measurement method over others used in the project.

(2) When individual laboratory results are published, the source organizations should not be linked to the results they provided.

6.17 *Storage Instructions*—Storage conditions (for example, temperature, exposure to light) necessary to maintain the validity of a CRM/RM material are important. If no special requirements apply, it is helpful to the user to state so.

6.18 *Instructions for Handling and Use*—Instructions for handling and use of the CRM/RM should be clear and concise. See also 6.12, which discusses how heterogeneity can affect use.

6.18.1 Examples of instructions for handling and use include: