Designation: E2972 – 15

Standard Guide for Production, Testing, and Value Assignment of In-House Reference Materials for Metals, Ores, and Other Related Materials[1]

This standard is issued under the fixed designation E2972; 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 document provides guidance for the implementation of procedures for preparation of in-house reference materials for analytical testing of metals, ores, slags, and other materials encountered within the metals and mining industries.

1.2 This guide is applicable to the production of reference materials only (usually for internal use) and does not apply to the production of certified reference materials (CRMs). Materials may include metals, alloys, minerals, geological materials, manufacturing intermediates, and byproducts. Samples may be in a number of physical forms including blocks, disks, rods, wires, chips, granules, powders, and liquids.

1.3 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E32 Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition (Withdrawn 2015)[3]

E34 Test Methods for Chemical Analysis of Aluminum and Aluminum-Base Alloys

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition

E88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E178 Practice for Dealing With Outlying Observations

E255 Practice for Sampling Copper and Copper Alloys for the Determination of Chemical Composition

E415 Test Method for Analysis of Carbon and Low-Alloy Steel by Spark Atomic Emission Spectrometry

E716 Practices for Sampling and Sample Preparation of Aluminum and Aluminum Alloys for Determination of Chemical Composition by Spectrochemical Analysis

E826 Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectrometry

E877 Practice for Sampling and Sample Preparation of Iron Ores and Related Materials for Determination of Chemical Composition and Physical Properties

E1086 Test Method for Analysis of Austenitic Stainless Steel by Spark Atomic Emission Spectrometry

E1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis

E1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition

E2857 Guide for Validating Analytical Methods

2.2 *ISO Standards:*[4]

ISO Guide 30 Terms and Definitions Used in Connection with Reference Materials

ISO Guide 30/Amd. 1 Revision of definitions for reference material and certified reference material

ISO Guide 35 Reference materials—General and statistical principles for certification

ISO Guide 98-3 Guide to the Expression of Uncertainty in Measurement (GUM: 1995)

ISO/IEC 17025 General requirements for the competence of testing and calibration laboratories

[1] This test method 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 Feb. 15, 2015. Published March 2015. DOI: 10.1520/E2972-15.

[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] The last approved version of this historical standard is referenced on www.astm.org.

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

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide, refer to Terminology E135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *development report, n*—document giving detailed information on the preparation of an in-house reference material and the methods of measurement used in obtaining the assigned values.

3.2.2 *in-house reference material, iRM, n*—reference material with documented homogeneity that is intended for use for quality control purposes, calibration, evaluation of a calibration, or standardization whose values may have limited traceability and for which rigorously derived uncertainty information is not mandatory.

3.2.3 *method of demonstrated accuracy, n*—test method for which proof of accuracy has been published even though it may not fall within the category of a reference method.

3.2.4 *metrological traceability, n*—property of a measurement result or the value of a reference material whereby it can be related, with a stated uncertainty, to stated references through an unbroken chain of comparisons.

3.2.5 *primary reference method, n*—analytical procedure that does not require the use of calibrants to achieve accurate results, rather the result is based on a defined physical constant or a derived physical constant.

3.2.5.1 *Discussion*—Examples include gravimetry, coulometry, specific titrimetric methods, and isotope dilution mass spectrometry. Each individual laboratory should validate its performance of such methods with reference materials.

3.2.6 *reference method, n*—thoroughly investigated method, clearly and exactly describing the necessary conditions and procedures for the measurement of one or more property values that has been shown to deliver accuracy and precision commensurate with its intended use and can therefore be used to assess the accuracy of other methods for the same measurement, particularly in permitting the characterization of an RM (ISO Guide 30).

3.2.6.1 *Discussion*—This includes all national or international standard methods, which may not be classified as primary reference methods because they are calibrated against standard solutions of pure chemical substances.

3.2.7 *uncertainty, n*—defined by ISO Guide 98-3 as a "parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand."

4. Significance and Use

4.1 This document provides guidance for the implementation of procedures for the preparation, testing, and documentation of an in-house reference material (hereafter called an iRM) to be used for a number of purposes, enumerated in the following document, associated with development, validation, and control of chemical and physical measurement processes.

4.2 This guide is primarily concerned with characterization of the chemical compositions of metals, ores, and related materials. For all these materials, there is a continuing, strong demand for reference materials (RMs) that is difficult for metrology institutes and private certified reference material (CRM) developers to meet because CRM development requires substantial investments of time and money. The metals and mining industries consume RMs and create new product and by-product compositions at high rates. They use analytical methods that provide rapid and accurate determinations, and both quality assurance and quality control can be maintained using efficient procedures provided appropriate iRMs are available.

4.3 The user of this guide must recognize that development of an iRM for any purpose carries with it the responsibility to design and execute the development process correctly, and to document the process thoroughly. In addition, the user of an iRM bears the responsibility for correct use of the iRM material within its design limitations.

4.4 This guide contains discussions on material selection and sampling for RMs with some attention given to conversion to the final forms.

4.5 The use of iRMs is appropriate for control chart procedures to demonstrate that chemical measurement processes are under statistical control. This function requires demonstration of sufficient homogeneity of a material, but it does not require assignment of chemical and physical property values with associated, exhaustively evaluated uncertainties.

4.6 The use of iRMs is appropriate for calibration of test methods and evaluation of calibrations in several ways, including checking for bias, systematic testing of corrections for matrix effects, and testing of sample preparation procedures. See Section 6. This guide provides explanations of general cases in which an iRM can be used as part of a validation process (see Guide E2857).

4.7 Because this document is a standard guide, it is intended to educate those who are involved in laboratory operation, quality system development and maintenance, and accreditation of laboratory operations within the scope of a quality system. However, this guide does not constitute requirements for assessment and accreditation.

5. Hazards

5.1 The preparation of metal RMs can involve hazards associated with melting, casting, heat treating, forging, atomizing, pickling, shot blasting, machining, and sampling.

5.2 Hazards may be encountered in crushing, grinding, and sieving particulate and powdered materials such as ores and related metallurgical materials.

5.3 For precautions related to the analysis of RMs, see Practices E50.

6. Uses of iRMs and Information Requirements Related to the Applications

6.1 *Process Control:*

6.1.1 For efficient, high throughput in a laboratory, chemical measurement processes, namely test methods, must be kept under statistical control. Perhaps the most convenient way to accomplish this control is to measure one or more materials at

appropriate time intervals. When the material(s) can be treated as a regular sample and taken through all steps of the process, the measured results easily can be used to demonstrate statistical control of the entire chemical measurement process.

6.1.2 A product-based material demonstrated to be sufficiently homogeneous can be prepared in sufficient quantity to enable its use for a long period of time. A sufficient level of homogeneity is defined as providing repeatability variance low enough to maintain a process control chart that ensures the uncertainty goals of the test method are met on a routine basis.

6.1.3 The material chosen for this purpose should be demonstrated to be stable for at least the length of time it will be used for control charts. For most metals and alloys, stability is known to be measured in years, if not decades. Stability of natural matrix geological and mineral materials may be less certain and may require monitoring. However, RM producers have demonstrated that mineral and geological materials can be processed and packaged in ways that provide long-term stability measured in years.

6.1.4 For process control, it is not necessary to develop values traceable to the International System of Units (SI) or any CRMs. The laboratory simply runs the material as a routine sample at least 20 times to establish a mean and repeatability standard deviation. These measurements should be carried out over a time period chosen with consideration to other factors affecting routine use of the test method. Refer to Practice E1329 for further guidance on the use of control charts.

6.2 *Drift Correction*—The purpose of a drift correction iRM is to provide stable, high-precision signals for the constituents of interest. In this case, it is not necessary to know the values of the amounts of the constituents. Homogeneity and stability should be demonstrated as above, but the calculations can be done in units of the measured phenomenon on which the instrumental or chemical technique is based. One example is the count rate of fluorescent X-rays obtained under the chosen measurement conditions.

6.2.1 To satisfy these requirements, it is necessary to have a stable, homogeneous material that can be used numerous times without degradation and that gives a strong measured signal for a high correction point or a low signal for a low correction point in the case of a two-point drift correction approach.

6.3 *Instrument Conditioning*—For certain test methods, the equipment must be stabilized and conditioned for use on a regular basis, typically daily. It is necessary to use materials similar in chemical and physical properties to the analysis samples, but it is not necessary to know accurately the compositions of materials used for conditioning.

6.3.1 It may be useful to have confidence that a conditioning material is homogeneous and stable. However, the purpose is to show that the instrument is ready for calibration, and the requirements for homogeneity and stability can be relaxed relative to the calibrants.

6.4 *Evaluation of Matrix Influence or Spectral Interference*—Both of these phenomena involve systematic effects of one constituent on another or on itself. To evaluate the magnitude of an effect, a laboratory may require a set of materials specially prepared to have known relationships among the values of the subject constituents within the set. That is, the value of Constituent A in Material X may be twice the value in Material Y and three times the value of Constituent A in Material Z. There may be multiple pairs of related constituents in a set of materials. The known relationships allow the laboratory to calibrate influence and interference coefficients empirically or to validate coefficients determined from first principles. An iRM for evaluation of matrix influence or spectral interference should have values obtained from an independent test method or multiple methods of analysis.

6.4.1 The materials in the set should be demonstrated to be sufficiently homogeneous to be sampled at the appropriate quantity and maintain the required ratios of constituent amounts with sufficient precision for the uncertainty goals of the test method.

6.4.2 Stability is a less stringent requirement because it is typical that the coefficient(s) need only be determined once, unless the instrumentation is modified significantly. This is convenient because it is known that some artificial sets of materials, even alloys, of this nature are unstable and may last for months instead of years.

6.5 *Calibration*—An iRM can be used as a calibrant in much the same way as a CRM. This is a key role because not all CRM producers can keep pace with the development of new alloys and the development or modification of manufacturing specifications.

6.5.1 An iRM used for calibration should have been developed with attention to homogeneity as with other uses of iRMs.

6.5.2 An iRM for calibration should have values obtained from independent test methods or multiple methods of analysis.

6.5.3 If the laboratory requires the same characteristics as provided by a CRM, the requirements are essentially the same as for development of a CRM by internationally accepted practices.

6.5.4 If the laboratory chooses to take a less stringent approach, the laboratory may assign values based on its own analyses, possibly with analyses from additional laboratories. Such approaches may not cover all aspects found in international standards and guides for RM development.

6.6 *Type Standardization*—Type standardization is often described as a form of drift correction. In fact, it is both a drift correction and a recalibration of the sensitivity of the calibration model. Laboratories use RMs to adjust a general calibration for a specific alloy or material type.

6.6.1 For example, spark atomic emission spectrometers can be calibrated to a range of alloys in a general category such as aluminum. There are hundreds of registered alloys whose compositions vary significantly. The general calibration defines matrix and spectral influence coefficients and the curve *x*-intercept. However it is difficult to define accurately inter-element corrections for each individual alloy given the number of alloys and possible composition ranges. The laboratory may use a RM of a similar composition to a particular alloy to adjust the sensitivity parameters of the calibration model for as many elements as are certified for the RM. This approach places utmost confidence in the certified values for the RM.

6.6.2 This approach is convenient in that it does provide drift correction by recalibrating the sensitivity values whenever samples of that alloy specification must be analyzed.

6.6.3 If there is not a CRM available with the required composition or if a CRM does not contain value(s) for key constituents, the laboratory may choose to develop an iRM, or it may choose to develop additional values for an available CRM.

6.6.3.1 Developing additional values for an existing CRM from an outside supplier requires the assumption that the homogeneity of the existing CRM for additional constituents can be adequately assessed using a small number of units of the CRM.

6.6.3.2 All such values and uncertainties developed without the knowledge or participation of the original developer of the CRM are of lesser quality, assuming the original developer complied with all international practices.

6.6.4 If the laboratory requires the same characteristics as provided by a CRM, the requirements for production of the iRM should be similar to those for development of a CRM by industry accepted practices.

6.6.5 If the laboratory chooses to take a less stringent approach, the laboratory may assign values based on its own analyses, possibly with analyses from additional laboratories.

6.6.6 In some cases, it may be necessary to obtain additional values for an RM or CRM when those values are needed to enable corrections for interferences in instrumental methods. In this case, traceability of the value(s) to the SI is not necessary because the values will be used only for making minor corrections, and the influence of uncertainty is low.

7. Production Sequence

7.1 Identify the need for an iRM. Confirm that a material of iRM quality would be fit for the intended purpose.

7.2 Specify the required form and composition, the desired manufacturing method, and the minimum quantity required.

7.3 Identify the source for the iRM.

7.4 Initiate the project documentation process.

7.5 Identify the processes required to convert the material to the desired form for use as an iRM.

7.6 Prepare the candidate iRM, including packaging and identification of all lots and sublots, if appropriate.

7.7 Develop an experimental plan for acceptance and homogeneity testing, including selection of test samples, designation of test methods, and specification of sample quantities for each test method.

7.8 Perform acceptance testing, including material homogeneity testing and evaluation of other characteristics, possibly including material stability.

7.9 Identify a suitable panel of test methods and analysts and provide instructions for the determinations.

7.10 Select samples of the material and of quality assurance materials and provide them to the analysts, along with instructions for reporting results.

7.11 Receive, tabulate, and perform a technical evaluation of the resultant data. Carry out necessary rework.

7.12 Write, review, and approve reports for all testing, as applicable.

7.13 Perform a statistical analysis of the data set to ensure it is appropriate for the intended purpose of the iRM.

7.14 Complete and approve all necessary documentation for the iRM, including a development report and a concise summary that provides the information necessary for the intended use of the iRM.

8. Factors Influencing the Specifications for the Finished In-house Reference Material

8.1 It is appropriate to set aside production materials having the same manufacturing specification and metallurgical history as the production materials they will subsequently be used to monitor. The desired composition may already be available in semi-finished form, such as an ingot, bar, or slab.

8.1.1 For analysis of metals, metallurgical condition is an important consideration. Instrumental techniques such as X-ray fluorescence, spark atomic emission, and glow-discharge atomic emission are usually used to measure samples in solid form with minimal sample preparation. These techniques may be subject to analytical bias caused by the metallurgical history of the alloy. It may be necessary to develop separate RMs for each of the metallurgical processes.

8.1.2 Cast materials that are rapidly quenched (namely, chill cast) may have the advantages of minimal grain size and improved homogeneity. However, it is necessary to characterize the extent (distance) within the material to which the improved properties extend.

8.2 It may be possible to obtain the desired material in finished form meeting the physical size requirement from a commercial source.

8.3 If a composition is to be made by a melting process, a detailed understanding of the metallurgical interactions between the added constituents and the matrix metal may be useful. In many cases, the more elements specified, the greater the difficulty in achieving the specification in a homogeneous material.

8.4 For particulate materials, it will be necessary to choose the optimum particle size range based on compositional and analytical requirements. Specially designed grinding and sieving may be necessary to obtain the required homogeneity.

8.5 Mineralogical materials often require specific drying instructions or ignition procedures to define adequately the form of the material to be analyzed and the basis for the assigned values of the constituents or properties.

8.6 Sterilization may be necessary for natural matrix materials for the purpose of destroying any microorganisms that may use components of the material as a food source or other resource. Bacterial action may convert an element to a volatile chemical form.

9. Sample Identification and Record-keeping

9.1 Material identification is required at all times during RM development.

9.1.1 Comprehensive sample identification ensures that unacceptable portions of a batch can be isolated from the usable portion.

9.2 Complete record-keeping is vital during the entire process of RM production. Laboratory quality system requirements may define the form and extent of records required for iRM development.

10. Acceptance Testing and Homogeneity Testing

10.1 Homogeneity testing (for example as described in Practice E826) is a crucial part of RM evaluation. All multi-element samples are heterogeneous, but the acceptable degree of heterogeneity for any element within a batch will be determined by the test method and sample size as well as by the degree of uncertainty that can be tolerated in the final certified value.

10.2 Homogeneity testing should include consideration of the quantity of RM needed for the intended purpose. Heterogeneity should be tested at or below the minimum quantity, typically minimum mass, per specimen in the test methods with which the iRM will be used.

10.3 If the purpose of the iRM includes use with more than one type of instrument (for example, spark atomic emission and X-ray fluorescence spectrometers), then samples of the candidate material should be analyzed on these instruments to confirm that comparable homogeneity results are obtained.

10.3.1 Instrumental methods measure the material in ways that define different shapes, areas, and depths in a specimen. These sampling characteristics may be affected to different degrees by material physical and chemical characteristics. For example, small spot measurements will be strongly impacted by areal inhomogeneity at or near the surface of a specimen. Large spot measurements may be insensitive to areal inhomogeneity on a smaller size scale.

10.4 *Sources of Inhomogeneity:*

10.4.1 For metal solids, heterogeneity can be the result of local segregation (usually caused by intermetallics, interstitial compounds, and multiple phases at the millimetre or sub-millimetr level), axial or circumferential segregation (which can arise during solidification or processing), or poor mixing before solidification (leading to compositional trends across the batch or lot).

10.4.2 In some metal mixtures and alloys, there may be stresses that result in diffusion of certain elements toward or away from the surface of a solid. The result is one or more concentration gradients extending from the surface into the solid on a length scale that may be similar in magnitude to the depth to which an instrumental technique obtains information. This depth may also influence any procedures for obtaining chips from a solid.

10.4.3 For ores, slags and other non-metals, local inhomogeneity can be caused by the presence of metal particles and multiple crystalline phases. There may also be random heterogeneity present in a batch that was not well mixed or was divided using a non-equal probabilistic method.

10.5 Wasted effort can be minimized by making preliminary heterogeneity checks before any downstream processing or testing. It may be necessary to design special test methods to evaluate heterogeneity of the bulk material before beginning serial production methods such as ingot to bar conversion; billet to bar conversion; and slicing or chipping for metals; or crushing, grinding, and splitting for ores and related materials.

10.6 All physically unacceptable portions of a batch, including zones containing visible inclusions, porosity, extraneous material, and so forth, should be removed. Detailed homogeneity testing should be performed on the remainder of the batch after it has been prepared into its final form.

10.7 For chill-cast material to be tested by spectrochemical methods, a study should be made to determine the usable depth and the radial and circumferential segregation within a bulk ingot, billet, or bar. The test locations evaluated should be selected to include possible metallurgical extremes.

10.8 For disks produced from wrought material or continuous cast bar, variability in all directions (radial, circumferential, and longitudinal) should be checked. It may be possible to accomplish this task using slices from the ingot or billet obtained before final cutting of units.

10.9 After cutting of final units, testing should cover within- and among-unit variability.

10.10 For powders, variability should be checked after rotary sample division and bottling. Again, within- and among-container variability should be evaluated.

10.10.1 Sieve at least one aliquot of the bulk material and arrange for the different size fractions to be analyzed to determine any variation in composition. Often, fine and coarse particle sizes will have compositions different from the bulk material. In such a case, it may be necessary to separate the fine and coarse sieve fractions. It may be of value to make separate RMs from these other sieve fractions.

10.11 If inhomogeneity is identified as being of significant magnitude with respect to either other sources of analytical uncertainty or to the overall uncertainty goals for the iRM, there are several possible courses of action.

10.11.1 When inhomogeneity of a material is comparable in magnitude to other sources of uncertainty, a standard uncertainty component for heterogeneity should be included in the overall uncertainty budget.

10.11.2 When inhomogeneity of a material is of greater magnitude than is acceptable given the required sample quantity or the overall uncertainty goal for a constituent, there are options.

10.11.2.1 The material can be scrapped and a new material sought.

10.11.2.2 The material can be separated into smaller sublots that exhibit sufficiently low heterogeneity. In this case, each sublot would be treated as a separate iRM.

10.11.2.3 The individual units of the candidate iRM can be given serial numbers, and their values can be specified individually or by number range.

10.11.2.4 Inhomogeneity may be observed within a unit, for example, gradients in chill cast material. It may be possible to define the relationship between values and depth to make the material useful. This is a difficult proposition and is not

recommended because uncertainty in the relationship between values and depth is typically prohibitive.

10.11.2.5 It may be more practical to give the user instructions to avoid sampling the unaccepted region.

11. Sampling and Material Preparation for Chemical Analysis

11.1 Prepare a procedure for obtaining test samples from the population of material.

11.1.1 There are two aspects to such a procedure. First, the bulk material should be properly subdivided and portioned into the planned individual iRM units. Second, individual iRM units should be selected from the prepared and perhaps packaged lot or sublots of candidate material for submission for analyses.

11.1.2 Guidelines for a suitable sampling procedure may be derived from Practices E32, E55, E88, E255, E716, E877, and E1806 and Test Methods E34, E415, and E1086.

11.1.3 Assistance from a statistician may prove valuable to ensure that the material is sufficiently well sampled for the test results to provide the necessary characterization of the batch of material.

11.2 All samples should be identified, and the corresponding sampling location should be noted, both on the sample and in associated documentation.

11.3 The amount of material required for each collaborating laboratory and test method should be estimated and the total calculated. Plan to prepare about double the estimated total to provide sufficient stock for contingencies such as segregation into smaller iRM lots, recheck analyses or additional test methods, if required.

11.4 *Obtaining Solid Samples from Bulk Solid Material for Use as a Solid iRM*—For iRMs to be issued as blocks or disks, specimens of suitable size should be sliced from the bulk material. Resulting pieces should be cleaned of cutting fluids and given a surface finish to remove gross imperfections from cutting tools. Final grinding or machining for instrumental measurements is considered to be part of the test method and the responsibility of the testing laboratory.

11.4.1 Use of instrumental techniques such as spark atomic emission or X-ray fluorescence may allow the homogeneity study and the quantitative analyses to be performed simultaneously. Practice E826 offers suggestions as to how this might be done.

11.4.2 After the homogeneity study, select a subset of the samples for use in the quantitative analyses.

11.5 *Preparing Chips from Bulk Solid Material for Use as a Chip RM*—Prepare chips by lathe or milling machine in a way that does not introduce contaminates to the chipss. Use a method that will produce, as much as possible, a constant chip size with acceptable morphology. Do not use a machining process that will cause chips to be overheated.

11.5.1 To facilitate chipping, it is sometimes necessary to anneal the solid material to a hardness that allows optimal chip preparation.

11.5.2 If necessary, solvent clean and air dry the chips.

11.5.3 Sieve the bulk material to eliminate the fines as well as the coarser particles. It is usually necessary to discard fine particles because of a significant difference in some of the elements of interest, such as carbon.

11.5.4 Store the material in airtight containers.

11.6 *Preparing Chips from Solid Material Intended for Use as a Solid iRM*—Prepare chips using a lathe or milling machine as described in 11.5 but do not sieve the chips to remove the large pieces or the fines. Analysts should be instructed to endeavor to use individual test specimens that contain all particle sizes in proportions representative of the entire contents of the container.

11.6.1 It may be useful to provide instructions for taking each test specimen, especially if the analysts will chip their own samples.

11.6.2 If analyses are to be made for oxygen, nitrogen, hydrogen, or any other element for which making chips may be detrimental, cut small solid samples from the bulk solid with minimal localized heating.

11.7 *Preparing Samples from Bulk Solid Material for Use as a Pin iRM*—Cut or shear the pins to the required weight. This requirement usually applies to any combination of the elements carbon, sulfur, nitrogen, oxygen, and hydrogen. Care should be taken to select a cutting method that does not contaminate the pins.

11.8 *Taking Powder Samples from Bulk Material*—Powder samples for quantitative analyses should be provided to analysts in the final, packaged form along with instructions explaining how the analysts should sample the contents of a package.

12. Plan for Quantitative Analyses

12.1 *Measurement Approaches*—For the highest quality, it is preferable to have two or more independent test methods performed on the material for each constituent or physical property of interest. Such an approach is intended to discover biases among methods and is necessary when all sources of uncertainty must be accounted for in the assignment of a value and uncertainty. Under some circumstances, it is not necessary to do everything possible to get as close as possible to the true value of the measurand. Then, a single, reliable test method can be used for each constituent.

12.1.1 *Measurement by Two or More Independent Reference Methods in One Laboratory*—Methods are regarded as independent if they are based on different chemical or physical principles. Instrumental methods are regarded as independent when the physical principle involved in the analytical signal or the mechanism of its production or both are different. Sample pretreatment for each method should minimize systematic error, but in some cases, the preparation methods may be similar. [**Warning—**If the sample pretreatment is not correctly performed (for example, if the same incorrect dissolution, separation, or preconcentration steps are used in otherwise independent methods), the measurements may yield well-matching, but biased results.]

12.1.2 *Measurement by a Single Primary Reference Method in a Single Laboratory*—This testing is usually performed by

two or more analysts working independently. Wherever possible, an accurately characterized second method should be used to provide additional assurance that the results are unbiased. Additional information on the measurement and statistics used in the certification of reference materials is available in ISO Guide 35.

12.1.3 *Measurement by a Single Instrumental Reference Method in a Single Laboratory*—This approach is based on acceptance of the test method as providing appropriate analytical quality for the intended use of the iRM. When appropriate, the method should be an accepted standard test method or it should be capable of producing accurate results similar in quality to the performance statements in a related standard test method.

12.1.4 *Measurement by a Network of Qualified Laboratories Using One or More Methods of Demonstrated Accuracy*—In general, this approach will provide consensus values that are good estimates of the true value of the measurand after a critical evaluation of all individual results. The minimum number of laboratories should be three for each element. This approach may offer the advantage of including a greater number of different test methods in the iRM development project.

NOTE 1—Laboratories can be regarded as qualified, if they satisfy one or more of the following criteria: *(1)* they are an experienced industry specialist with documented procedures to perform the work, *(2)* they are an independent laboratory with a satisfactory performance record for similar work, or *(3)* they have accreditation to ISO/IEC 17025 for the analytical work in hand.

12.2 The organizer of the interlaboratory analysis program may specify the use of a specific method or methods to participating laboratories when well-established standard measurement procedures are available. Such a requirement would usually be necessary for mineral-specific RMs. Alternatively, each participating laboratory may use the method of its choice provided that there is evidence of the validity of such a method.

12.3 The organizer of the interlaboratory analysis program may wish to request that cooperating laboratories make replicate determinations to improve the estimate of measurement uncertainty. If so, three replicate determinations per unit are the absolute minimum. All replicate determinations should be made on separate test portions. Multiple, freshly prepared surfaces on a single specimen of disk or block form metal can be considered separate test portions. However, they provide only within unit variability. Multiple blocks or disks should be tested to capture material variability completely.

12.4 For quality assurance materials, it is acceptable to require four separate determinations from a single unit of the material.

12.5 The organizer should provide an approximate composition of each candidate material and advise participants of any special instructions for preparation, such as time and temperature for drying powder samples.

12.6 Participating laboratories should be required to report individual results (not just the average). The number of significant figures reported should comply with the guidelines for the program, normally to include at least one more digit than will be needed in the consensus value

12.7 If traceability to specific calibrants is required, the organizer should provide samples of those calibrants along with the candidate sample(s).

12.8 *Check Analysis Procedure*—The data should be assessed for outliers. Ideally, the assignable cause for any outlier should come from the laboratory that produced the outlying value. Refer to Practice E178 for a method of dealing with outlying observations. It is recommended that the participating laboratory be informed for its benefit and be invited to repeat their test program.

13. Critical Evaluation of Results and Calculations of Values and Uncertainty Estimates

13.1 See 10.11 for a discussion of the consequences of inhomogeneity in a candidate material. The topic was discussed in 10.11 because it applies to material acceptance considerations and instructions given to analysts for quantitative determinations.

13.2 When quantitative analytical measurements have been completed, the data should be thoroughly reviewed to ensure that variances for the analytes are acceptable and there are no obvious biases among analytical methods and laboratories.

13.3 Suspect results should be investigated and validated. The preferred approach is to retain any suspicious results until an assignable cause can be found for the problem.

13.3.1 Review the results for quality assurance materials. Poor performance here can be considered a cause for suspect results.

13.4 The final assigned values may be obtained by a documented calculation procedure.

13.4.1 Because there are a wide range of uses for iRMs, the range of available calculations is also broad. Procedures range from simple mean or median values to complex approaches with weighted means and bootstrap estimations of uncertainty.

13.4.2 Experience has shown that relatively straightforward approaches are preferable for obtaining reference values, typically including mean and median values with or without weighting.

13.4.3 Refer to ISO Guide 98-3 for information on the statistical treatment of analytical data.

NOTE 2—ISO Guide 35 provides additional information on homogeneity testing and statistical treatment of data.

14. Uncertainty of the Assigned Value

14.1 This section is an extension of discussions in Section 6 of the required characteristics of iRMs used for various purposes. Laboratories should consider the intended use of the iRM being developed when determining the acceptable magnitude of the final uncertainty of each value and the extent to which the uncertainty will be evaluated. iRMs intended for use in calibration or type standardization require more rigorous evaluation of the uncertainty than iRMs intended only for use in process control procedures.

14.2 This section is also an extension of the discussion in Section 12 of the various approaches to analyzing an iRM. In all cases, the uncertainty of a constituent value should be informed by the precision and bias in the quantitative analytical

results. Here again, ISO Guide 98-3 and Supplement 1 are informative of approaches to calculating uncertainty. It is beyond the scope of this guide to provide details of procedures for estimation of uncertainty and expression of a final uncertainty for a given value. What is given herein is a brief discussion of the requirements from each of the analysis approaches discussed in Section 12.

14.2.1 For each test method used laboratories should obtain all sources of uncertainty from the test method and include them in a combined value. Besides the typical sources of uncertainty discussed in numerous references on the topic, the laboratory should include the uncertainty of the calibrant(s).

14.2.2 Laboratories that use multiple methods from one or more laboratories should consider the precision of each laboratory/method data source and the biases among the data sources.

14.3 After technical evaluation of the results, the laboratory assigning the value(s) to the iRM may use a confidence interval, at a specified confidence level, as the final uncertainty for the assigned value.

14.4 The definition of the final uncertainty should be included in the iRM documentation.

NOTE 3—ISO Guide 35 provides additional information on evaluating measurement uncertainty.

15. RM Documentation

15.1 Documentation should be formatted for ease of reference. The essential features of the documents are as follows:

15.1.1 Product identification, type, and form;

15.1.2 Intended use and instructions for use, including the minimum quantity needed for results consistent with the assigned values and their uncertainty estimates, and instructions for mixing, sampling, cleaning, drying, or igniting;

15.1.3 Summary of manufacturing history, including source information, if appropriate;

15.1.4 Summary of homogeneity testing (method(s), sampling details, pass/fail criteria), and results;

15.1.5 Individual analytical results in tabulated form:

15.1.5.1 This feature is optional, and it is not recommended for documents that will be made public because users may be tempted to focus only on results from a preferred test method.

15.1.5.2 Tabulated results may be useful when it has been determined that users may focus on method-specific values.

15.1.6 Final assigned values and estimated uncertainties with definitions of the measurands and uncertainties, as appropriate;

15.1.7 A list of the collaborators;

15.1.8 Tabulation of the analytical methods used;

15.1.9 Requirements for storage, shelf life, and expiration date:

15.1.9.1 Consider setting an expiration date for the iRM based on knowledge of the inherent stability of the material and any accelerated aging test data obtained.

15.1.9.2 It is acceptable to state that the iRM is valid indefinitely based on continued monitoring or behavior of similar material.

15.1.9.3 It is acceptable to extend the period of validity on the basis of continued successful use of the iRM or after performing additional stability testing in the future.

16. Archival Procedure

16.1 Each iRM should have a secure file in which all records relating to the iRM are stored.

16.1.1 This file should be preserved for a defined period consistent with the organization's quality system requirements.

16.2 Wherever practicable, one or more units of the iRM should be preserved in case any retrospective testing is required.

17. Keywords

17.1 drift correction; homogeneity; in-house reference material; quality assurance; quality control; reference material development; standardization; uncertainty estimation; value assignment