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Standard Guide for Production, Testing, and Value Assignment of In-House Reference Materials for Metals, Ores, and Other Related Materials¹

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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- E32 Practices for Sampling Ferrous Alloys and Steel Additives for Determination of Chemical Composition (Withdrawn 2015)³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

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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.