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Standard Guide for
Testing and Certification of Metal, Ore, and Metal-Related Reference Materials[1]

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1. Scope

1.1 This guide describes procedures to be considered for the testing and certification of metal, ore, and metal-related reference materials in the form of blocks, disks, rods, wires, chips, and powders.

1.2 *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:*

E 32 Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition[2]

E 34 Test Methods for Chemical Analysis of Aluminum and Aluminum-Base Alloys[2]

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores and Related Materials[2]

E 55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition[2]

E 59 Practice for Sampling Steel and Iron for Determination of Chemical Composition[2]

E 88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition[2]

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[2]

E 178 Practice for Dealing with Outlying Observations[3]

E 255 Practice for Sampling Copper and Copper Alloys for the Determination of Chemical Composition[2]

E 350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron[2]

E 351 Test Methods for Chemical Analysis of Cast Iron—All Types[2]

E 716 Practices for Sampling Aluminum and Aluminum Alloys for Spectrochemical Analysis[2]

E 826 Practice for Testing Homogeneity of Materials for the Development of Reference Materials[2]

E 877 Practice for Sampling and Sample Preparation of Iron Ores and Related Materials[2]

E 1019 Test Method for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and Iron[2]

2.2 *ISO Standards:*

ISO Guide 30 Terms and Definitions Used in Connection With Reference Materials[4]

ISO Guide 31 Contents of Certificates of Reference Materials[4]

ISO Guide 33 Uses of Certified Reference Materials[4]

ISO Guide 35 Certification of Reference Materials—General and Statistical Principles[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide, refer to Terminology E 135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *certification report*—a document giving detailed information, supplementary to that contained in a certificate, on the preparation of the material and the methods of measurement used in obtaining the certified value(s) for a given reference material. It includes a summary of the results obtained (including a description of all factors affecting accuracy) and a description of the way in which the results were treated statistically.

3.2.2 *certified reference material (CRM)*—reference material accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realization of the unit in which the property values are expressed; each certified value is accompanied by an uncertainty at a stated level of confidence (from ISO Guide 30).

3.2.3 *certifying body*—a technically competent body (organization or firm, public or private) that issues a reference material certificate which provides the information detailed in ISO Guide 31.

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[2] *Annual Book of ASTM Standards*, Vol 03.05.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] Available from American National Standards Institute, 11 West 42nd St., 13th Floor, New York, NY 10036.

3.2.4 *comparative analytical method*—an analytical procedure that requires the use of CRMs, reference materials (RMs), or, in certain instances, primary chemical standards for calibration. Methods vary widely in the number of such CRMs required and the degree to which such CRMs must match unknown samples.

3.2.5 *definitive analytical method*—an analytical procedure that does not require the use of CRMs, RMs, or primary chemical standards to achieve accurate results. Examples include gravimetry, coulometry, specific titrimetric methods, and isotope dilution mass spectrometry. Each individual laboratory should validate its performance of such methods with CRMs, RMs, or primary chemical standards.

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

3.2.7 *primary chemical standard*—a pure metal or a compound of sufficient high purity to permit its use in the calibration or validation of analytical methods.

3.2.8 *reference material (RM)*—a material or substance, one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

3.2.9 *reference material certificate*—a document stating one or more property values and their uncertainties and confirming that the necessary procedures have been carried out to establish their validity and traceability. A reference material certificate is an essential attribute of CRM.

3.2.10 *reference method*—a 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 have accuracy and precision commensurate with its intended use and can be used to assess the accuracy of other methods for the same measurement, particularly in permitting the characterization of an RM. This includes all national or international standard methods, which may not be classified as definitive methods because they are calibrated against standard solutions of pure chemical substances.

3.2.11 *traceability*—property of a result of a measurement whereby it can be related, with stated uncertainty, to stated references, usually national or international standards, through an unbroken chain of comparisons (ISO Guide 30).

3.2.12 *uncertainty of a certified value*—the range of values within which the "true" value is asserted to lie with a stated confidence.

3.2.13 *validation (of an analytical method)*—evidence that a method yields accurate results on a test sample because it yields accurate results on a CRM of similar composition which was analyzed at the same time.

4. Significance and Use

4.1 This guide describes the suggested procedures for the preparation, testing, and certification of reference materials (RMs) to be used in the calibration, verification, and control of methods used to characterize the chemical composition of metals, ores, and related materials.

4.2 Certified reference materials are frequently rare and valuable commodities requiring investment of considerable cost and production time. They are frequently available for only a limited portion of a user's range of interest.

4.3 When comparative analytical methods are employed, appropriate CRMs are often unavailable for calibration. In this case, the use of RMs is indicated as the alternative choice.

4.4 The use of uncertified homogeneous materials is appropriate for control chart programs where relative data consistency is being monitored. The use of CRMs for such purposes is often a misuse of valuable CRM stocks, especially when uncertified materials of suitable homogeneity are available. For information on the use and misuse of CRMs, see ISO Guide 33 and NBS Special Publication 260-100.[5]

4.5 Use CRMs and RMs with caution in the validation of analytical methods. The danger involves a potential for undetected systematic error, since the same methodology being validated may have been used to establish the values for the CRMs or RMs. For more information on the use of CRMs in the validation of analytical methods, see NIST Special Publication 829.[6]

5. Hazards

5.1 The preparation of reference materials involves hazards associated with the melting, annealing, casting, sampling, forging, rolling, atomizing, pickling, shot blasting, and machining of metal. Similarly, hazards are encountered in crushing, grinding, and sieving particulate and powdered materials.

5.2 For precautions related to the analysis of reference materials, see Practices E 50.

6. Justification of Production

6.1 Reference materials are needed to calibrate, verify, and control instrument methods when sufficient certified reference materials of the required composition or form, or both, are not available from certifying bodies.

6.2 Alloy types or grades not available from any certifying body are often needed to match the composition to be tested.

6.3 A study should be made to estimate the cost of RM production and testing. It is important that users remain aware that the preparation of RMs has an associated cost based on factors such as material cost, facility usage charges, personnel labor rates, outside laboratory fees, and so forth, in which the material cost is, in general, the lowest. For complex compositions, the cost of preparing RMs to match the composition of test samples can exceed that of available CRMs. In these cases, the use of CRMs is recommended.

6.4 A study of the costs associated with the RM production should take into account the amount of usable material compared to the total amount produced. It may be necessary to produce twice as much raw material in order to obtain the target amount of usable RM.

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[5] NIST Special Publication 260-100, *Handbook for SRM Users* (1993 ed.). Available from NIST, U.S. Department of Commerce, Gaithersburg, MD 20899.

[6] NIST Special Publication 829, *Use of NIST Standard Reference Materials for Decisions on Performance of Analytical Chemical Methods and Laboratories*. Available from NIST.

7. Types of Reference Materials and Reference Material Forms Covered in This Guide

7.1 *Reference Materials*:

7.1.1 *Multielement Reference Material*— Certified for a complete composition (may or may not include trace element composition).

7.1.1.1 *Grade-Specific Reference Material*— Meets or is close to the compositional specification for all elements of a particular grade of material.

7.1.1.2 *Drift-Correction Reference Material*—A cast or wrought material evaluated for an array of elements, useful for drift correction of instrumental methods. A drift-correction RM may conform to a compositional specification.

7.1.2 *Element-Specific Reference Material*—Certified for a small number of elements. A common type of element-specific RM consists of chips or pins certified for carbon, sulfur, nitrogen, oxygen, or hydrogen, or a combination thereof.

7.2 *Reference Material Forms*:

7.2.1 *Monolithic Solids*:

7.2.1.1 Castings,

7.2.1.2 Wrought material finished to bar form, and

7.2.1.3 Rod and wire material.

7.2.2 *Particulates*:

7.2.2.1 Chips, and

7.2.2.2 Powders.

NOTE 1—In many cases, full composition data, although not necessarily certified, will be needed to permit corrections for interferences in various instrumental methods, especially for critical elements at low concentrations.

8. Specifications for the Finished Reference Material

8.1 If a composition is to be made by a melting process, a realistic approach should be taken when determining the number of elements and their concentrations in each RM. 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 is necessary. In most cases, the more elements specified, the greater the difficulty in achieving the specification. Even the creation of a single element RM, such as sodium in an aluminum matrix, may be very difficult to produce.

8.2 The finished composition may be available in semi-finished form, such as an ingot or a larger-than-specified bar or slab form. A study should be made to determine the requirements for processing to the final form.

8.3 The material may be available in finished form, meeting the physical size requirement, within the plant, within the corporation, or from commercial sources.

8.4 Metallurgical condition is an important consideration. Most instrumental techniques such as X-ray fluorescence, spark optical emission, and glow-discharge optical emission use RMs in their solid metallic form. One or more of these methods may be subject to analytical bias due to the sample's metallurgical history. In order to minimize the influence of metallurgical effects, the unknown sample being analyzed should have the same metallurgical structure as the RM being used to calibrate the instrument response. Some instruments may require separate calibrations for cast, chill cast, and wrought materials. For example, in the analysis of iron base metals, X-ray fluorescence is subject to thermal history effects if the heat treatment causes the precipitation of a second phase and affects the homogeneity of the material.

9. Production to Final Form

9.1 This guide will not specify the procedures used for melting or production of the RM into the final form. Methods will vary in accordance with composition requirements.

9.2 Some portions of the candidate material may need to be discarded if homogeneity testing indicates the material is not uniform.

10. Sample Identification and Recordkeeping

10.1 Material identification is required *at all times* during RM production, especially during random sampling for the homogeneity testing. Proper sample identification will ensure that unacceptable portions of a candidate material may be isolated from the usable portion.

10.2 Proper recordkeeping is vital during the entire process of the RM production, from the initial determination of the need to produce an RM, to the preparation of the analysis report.

11. Homogeneity Check

11.1 Estimate the amount of acceptable inhomogeneity prior to the production of the material. The homogeneity testing procedure shall be designed to test at least the minimum sample size or test area required for its intended use.

11.2 Homogeneity testing is a crucial part of RM evaluation. Costs can be held to a minimum if a preliminary homogeneity test, as described in Practice E 826, is performed before expensive fabrication and extensive testing is undertaken. It may be necessary to design special test methods to evaluate homogeneity of the bulk material prior to beginning serial production methods such as ingot to bar, billet to bar, and bar to chips.

11.3 Perform the homogeneity test on the candidate material after it is produced to its final form and all physically unacceptable portions (containing visible inclusions, "pipe," scale, and so forth) have been discarded.

11.4 A test for trend inhomogeneity should be done before random inhomogeneity is evaluated. The samples, however randomly selected, must keep traceability to their original location to avoid loss of trend inhomogeneity information. When trend inhomogeneity is detected, appropriate measures should be performed with the candidate material, such as discarding the extreme parts and subdividing the bulk.

11.5 For chill-cast material to be used by spectrochemical methods, a study should be made to determine the usable depth and the radial and circumferential segregation. The test pieces evaluated should be selected to represent possible metallurgical extremes.

11.6 For disks produced from wrought material and by direct casting, examine center to edge (radial) and circumferential variability in addition to piece to piece variation.

12. Pretesting Evaluation

12.1 If the RM is designed for use by more than one type of instrument (for example, optical emission spectrometer and X-ray fluorescence spectrometer), analyze samples of the candidate material on these types of instruments to determine if comparable analyses are obtained. If the analyses are acceptable, then proceed to 12.2.

12.2 In cases of RMs that require analysis for residual elements, conduct a preliminary screening by optical emission spectroscopy or mass spectrometry techniques, and record the results.

13. Sampling and Material Preparation for Chemical Analysis

13.1 Distribute a written sampling procedure to all sampling personnel. Practices E 32, E 55, E 59, E 88, E 255, and E 877 may be useful in determining a sampling procedure. Sampling sections of analytical methods such as Test Methods E 34 and Practices E 716 may also be useful. Maintain sample identification at all times. Record the location or locations where the bulk sample used for chemical analysis was obtained.

13.2 After homogeneity testing has proved the material satisfactory for the required use, a portion of the bulk material should be sampled and prepared for distribution to the testing laboratories.

13.3 Determine the sample size to distribute. Estimate the amount of material required for each laboratory and calculate the total. Plan to obtain double the calculated total to provide material sufficient for reserve stock and for recheck analysis, if required.

13.4 *Chips from Bulk Solid Material for Ultimate Use as a Chip RM*—Remove and discard any scale or surface oxide. Prepare chips by lathe or milling machine in a manner to avoid, as much as possible, a large variation in chip size. It is sometimes desirable to anneal material to a hardness which optimizes chip size during machining. Solvent clean and air dry. Store the material in an airtight container. For long-term storage, atmospheres of nitrogen or argon may be useful. It may be necessary to discard fine particles because of a significant difference in some of the elements of interest, such as carbon. Analyze the different sieve fractions for the elements to be certified.

13.5 *Chips from Bulk Solid Material for Ultimate Use as a Block, Disk, or Rod RM*—Prepare chips by lathe or milling machine in a manner to avoid, as much as possible, a large variation in chip size. Do not sieve the chips to remove the large or very small chips. Do not produce overheated chips during machining. Analysts should be instructed to use test portions which reflect all particle sizes in the test sample to ensure that the chip size variation is represented in the portion weighed for chemical analysis. If analyses are to be made for oxygen, nitrogen, or hydrogen, or any other element for which making chips would be detrimental, small solid samples shall be cut from the bulk solid with minimal localized heating.

13.6 *Samples from Bulk Solid Material for Ultimate Use as a Pin RM*—Use for any combination of the elements carbon, sulfur, oxygen, and nitrogen. Cut or shear the pins to the required weight.

13.6.1 Preliminary testing on samples taken from each end and the middle of the coil should be done before the coil is processed into pins. Test the bulk material used to produce pin material for homogeneity after the entire coil is processed into pins. After the pins have been thoroughly mixed, obtain random samples for homogeneity testing.

13.7 *Powder Samples from Bulk Material*:

13.7.1 Blend bulk material thoroughly before and after sampling.

13.7.2 Sieve bulk material and the different size fractions analyzed to determine if certain ranges of particle sizes yield discrepant results. Often, the very fine and very large particle sizes will show a significantly different analysis than the mid-range size material. It may be necessary to discard or segregate the fine and large particle sizes. If saved, the fine and large particle sizes may find use as a separate candidate RM material.

13.7.3 The selected fraction(s) should be riffle sampled to collect material to be distributed for chemical analysis. For some materials, packing in inert gas may be required.

13.7.4 Store the bulk powder in a sealed container to prevent absorption of moisture from the air.

13.7.5 Check periodically on the powder in bulk containers and smaller containers to ensure that the composition of the material has not changed due to moisture or other reasons. Record inspection details and results for placement in the RM archival file.

13.7.6 Always dry powder samples prior to analysis. Information on drying time and temperature shall be provided to the users.

14. Plan for Chemical Analysis

14.1 *Measurement Approaches*:

14.1.1 *Measurement by a Single Definitive Analytical Method in a Single Laboratory*—This test method is usually performed by two or more analysts working independently. Frequently, an accurately characterized second method is employed to provide additional assurance that the data are correct. Additional information on measurement and statistics used in the certification of reference materials is available in ISO Guide 35.

14.1.2 *Measurement by Two or More Independent Reference Methods in One Laboratory*—Methods are regarded as independent if they are based upon 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 shall be free of systematic error. The methods have small estimated inaccuracies relative to the analytical requirement.

NOTE 2—If the sample pretreatment is not correctly performed (for example, if the same incorrect dissolving, separation, or preconcentration steps, or a combination thereof, are used in otherwise independent methods) the measurements may yield well-matching, but totally erroneous results.

14.1.3 *Measurement by a Network of Qualified Laboratories Using One or More Methods of Demonstrated Accuracy*—In general, this approach will provide a good estimate of the actual true value and uncertainty of the result. The minimum number of laboratories should be three per elemental analysis.

14.1.3.1 A population of laboratories should exist that is uniformly capable of determining the analysis of the RM to provide results with acceptable accuracy.

14.1.3.2 Each laboratory mean is considered to be an unbiased estimate of the analysis of the material. This may not be true when instruments in several laboratories are calibrated with the same CRMs and RMs.

14.2 The organizer of an interlaboratory RM-evaluation program must designate the consenting laboratories which will participate. The organizer is responsible for establishing time schedules for sample distribution and return of test results.

14.3 The organizer of an interlaboratory RM-evaluation program may specify the use of a specific method or methods to participating laboratories when well-established standard measurement procedures are available. Such methods for steel and iron are Test Methods E 350, E 351, and E 1019. Otherwise, the organizer should allow each participating laboratory to use the method of its choice, provided that there is evidence of the validity of such methods.

14.4 If the results of the interlaboratory program are to serve as a final confirmation of the homogeneity of an RM, a sufficient number of laboratories shall be used and the analysis by each laboratory should be performed on duplicate units of the laboratory sample. The duplicate samples shall originate from different portions of the material. Otherwise, one unit for each participating laboratory may be sufficient.

14.5 Three replicate determinations per unit are the absolute minimum number of replicates on which valid "within laboratory" statistics can be performed. All replicate determinations shall be made on separate test portions.

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

14.7 Participating laboratories should be requested to report individual results (not just the average). The number of significant figures reported should comply with the guidelines for the program and, in general, include at least one more digit than will be used in the grand average. Participating laboratories should be provided with an outline of the measurement procedure, including literature references where appropriate, in sufficient detail to permit an understanding of all preliminary stages in the measurement process.

14.8 If CRMs are available, the organizer should require that at least one, and preferably more, CRMs of similar composition certified for all the elements of interest, be analyzed as an unknown along with the candidate RM to show traceability to specific CRMs and to validate the analytical procedures. If a participating laboratory lacks an appropriate CRM for validation and traceability, one should be provided. If CRMs are not available, primary chemical standards or RMs may be used.

14.9 *Check Analysis Procedure*:

14.9.1 The results should be checked for technically explainable outliers which are excluded before any statistical evaluation is performed. The assignable cause for the outlier should ideally come from the laboratory that produced the outlying data. Refer to Practice E 178 for a method of dealing with outlying observations. If possible, it is recommended that the participating laboratory be informed for its benefit and be invited to repeat their test program.

14.9.2 When practical, data from several different instrumental analytical methods may prove useful in detecting possible biases.

15. Traceability of Analytical Evaluation

15.1 It is important to show that the specified analysis of the RM is traceable to one or more CRMs, if available. When no CRMs are available, RMs may be used. The CRMs or RMs used by participants in the testing process shall be sufficiently similar (in matrix) to the actual sample to be analyzed so as to include all analytical problems which might cause errors in the determinations.

15.2 Traceability of analysis may be achieved by using CRMs or RMs, or both, for method validation or using CRMs or RMs, or both, for instrument calibration.

15.2.1 The CRMs or RMs, or both, used for method validation must not be part of the calibration of the method. The user should apply to the CRMs and RMs exactly the same analytical procedure as for the unknown sample.

15.2.2 The CRMs used for instrument calibration shall be supplied with a certificate of analysis. The certificate of analysis or certification report should state the certified values and, if possible, the estimate of uncertainty or confidence interval. If it is necessary to use RMs due to a lack of sufficient CRMs, then the RMs selected for the calibration must be supplied with a certificate of analysis or certification report which should state the assigned value/values and the estimate of uncertainty or confidence interval.

15.3 The burden of proof of traceability to CRMs or RMs, or both, is on the organization making the traceability statement.

15.4 Within the United States, all balances used for chemical analysis must have their calibration traceable to NIST. Outside the United States, all balances should have their calibration traceable to NIST or to a nationally accredited calibration service.

16. Compilation of Data

16.1 When the chemical analysis is completed, the data will be thoroughly reviewed to ensure that variances for the analytes fall within the expected tolerances and that no biases were identified.

16.2 Certified values may be obtained by arithmetic average of the accepted data.

16.3 Where possible, a statistically derived estimate of uncertainty should be calculated for each analyte.

16.4 Refer to ISO Guide 35 for information on the statistical treatment of the analytical data.

17. Preparation of Certificate of Analysis

17.1 For information about details that can be included on a certificate of analysis, refer to ISO Guide 31.

18. Certificate of Analysis Revision

18.1 Certificates of analysis shall be revised to correct analytical or typographical errors or to add technical or editorial information.

18.2 Establish the need for a certificate revision by consensus of the initiators or users of the RM.

18.3 Upon completion of the revised certificate, a new certificate date shall be assigned to the certificate of analysis.

18.4 A statement shall appear on the certificate of analysis explaining the reason for the revision.

18.5 The revised version shall be appended to the file containing all records of the RM.

19. Archival Storage

19.1 Each RM shall have a file where all records relating to the RM are securely stored. The archival file shall be preserved for a period of not less than 30 years from the date the use of the RM has been discontinued.

19.2 Any paperwork relating to a RM shall be added to the archival file.

20. Keywords

20.1 certification; certified reference materials; reference materials

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