Designation: E826 – 14

Standard Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectrometry[1]

This standard is issued under the fixed designation E826; 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 practice is suitable for testing the homogeneity of a metal lot or batch (L/B) in solid form by spark atomic emission spectrometry (Spark-AES). It is compliant with ISO Guide 35—Certification of Reference Materials: General and Statistical Principles. It is primarily intended for use in the development of reference materials but may be used in any other application where a L/B is to be tested for homogeneity. It is designed to provide a combined study of within-unit and between-unit homogeneity of such a L/B.

1.2 This practice is designed primarily to test for elemental homogeneity of a metal L/B by Spark-AES. However, it can be adapted for use with other instrumental techniques such as X-ray fluorescence spectrometry (XRF) or atomic absorption spectrometry (AAS).

NOTE 1—This practice is not limited to elemental analysis or techniques. This practice can be applied to any property that can be measured, for example, the property of hardness as measured by the Rockwell technique.

1.3 The criteria for acceptance of the test specimens must be previously determined. That is, the maximum acceptable level of heterogeneity must be determined on the basis of the intended use of the L/B.

1.4 It is assumed that the analyst is trained in Spark-AES techniques including the specimen preparation procedures needed to make specimens ready for measurements. It is further assumed that the analyst is versed in and has access to computer-based data capture and analysis. The methodology of this practice is best utilized in a computer based spreadsheet.

1.5 This practice can be applied to one or more elements in a specimen provided the signal-to-background ratio is not a limiting factor.

1.6 This practice includes methods to correct for systematic drift of the instrument with time. (**Warning—**If drift occurs, erroneous conclusions will be obtained from the data analysis.)

1.7 This practice also includes methods to refine estimates of composition and uncertainty through the use of a type standard or multiple calibrants.

1.8 It further provides a means of reducing a nonhomogeneous set to a homogeneous subset.

1.9 *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]

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

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E178 Practice for Dealing With Outlying Observations

E634 Practice for Sampling of Zinc and Zinc Alloys 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

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

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

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

2.2 *ISO Standard:*[3]

ISO Guide 35 Certification of Reference Materials: General and Statistical Principles

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

Current edition approved April 1, 2014. Published June 2014. Originally approved in 1981. Last previous edition approved in 2013 as E826 – 08 (2013). DOI: 10.1520/E0826-14.

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

[3] Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, Case postale 56, CH-1211, Geneva 20, Switzerland, http://www.iso.ch.

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology E135, and Practices E177, E178, E1329, and E1806.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *ANOVA (analysis of variance)*—a statistical means of partitioning the variance of a data set into contributing components.

3.2.2 *batch*—a set of specimens to be tested for homogeneity, often a subset of a lot.

3.2.3 *between-unit homogeneity*—homogeneity with respect to the various specimens in the candidate L/B (see Section 8).

3.2.4 *drift*—a gradual, systematic change in instrument readings with time.

3.2.5 *fair (fairness)*—the assurance for a participant in a proficiency test program that all of the material from which the participants' test materials are taken is sufficiently homogeneous so that any results later identified as outliers should not be attributed to any significant test item variability.

3.2.6 *homogeneity—as defined in this practice*, statistically acceptable differences between means in the test.

3.2.7 *solid form*—specimens are in a form equivalent to that described in 6.4.4 of Practice E1806.

3.2.8 *type standard—as defined in this practice*, calibrant similar in composition to the candidate for homogeneity testing.

3.2.9 *unit*—specimen to be tested, referred to as a disk, regardless of the actual shape.

3.2.10 *within-unit homogeneity*—homogeneity with respect to an individual specimen (see Section 8).

4. Summary of Practice

4.1 This practice, which is based on statistical methods (**1-8**),[4] consists of stepwise instructions for testing the homogeneity of a candidate L/B. The candidate specimens are selected as described in Section 10, and then measured by Spark-AES (Section 11). The resultant data are corrected for instrumental drift, if desired (see Sections 13 – 15), and then tabulated (see Tables 2, X1.3, and X1.4) to facilitate the statistical calculations that are performed according to Section 12.

4.2 The homogeneity of the L/B is determined from the results of the data analysis consisting of a one-way analysis of variance (ANOVA).

4.3 This practice *requires* that repeated measurements on the same position or specimen (P/S) have sufficient precision (that is, repeatability) through appropriate selection of instrumental parameters so that any significant difference within or between positions or specimens can be detected with confidence. This is best done through the use of drift management: standardization, control charts (Practice E1329), normalization, and drift monitoring.

4.4 This practice requires that there be an absence of outliers in the data (Practice E178). (**Warning—**The use of Practice E178 dealing with outliers should be done with extreme care to ensure that values are not discarded that may be valid for the analysis.)

4.5 Variability introduced by sample preparation may influence the findings of this practice.

5. Significance and Use

5.1 The purpose of this practice is to evaluate the homogeneity of a lot of material selected as a candidate for development as a reference material or certified reference material, or for a L/B selected for some other purpose (see Appendix X1 – Appendix X4 for examples).

5.2 This practice is applicable to the testing of samples taken at various stages during production. For example, continuous cast materials, ingots, rolled bars, wire, etc., could be sampled at various stages during the production process and tested.

6. Summary of the Test Method

6.1 *General*—This practice is based on J. W. Tukey's HSD (honestly significant difference) procedure for pairwise comparisons among means (**8**). It uses the ANOVA technique to partition the variation into contributing components, then eliminates contributions from sources other than heterogeneity and random processes. The model used is:

$$x_{ij} = \mu + \beta_i + \tau_j + \varepsilon_{ij} \quad (1)$$

where:

x_{ij} = the result of the ith burn on the jth P/S,
μ = the "true" mean of the population of all possible burn results,
β_i = the variation in the ith burn due to the measurement process,
τ_j = the variation in the jth P/S due to heterogeneity, and
ε_{ij} = the variation due to random or randomized processes.

6.1.1 The data are then arranged in a b by t matrix (where b is the number of burns per P/S and t is the number of positions or specimens) and rowwise statistics taken. These statistics allow the estimation and elimination of the variation due to the measurement process, leaving only the contributions from heterogeneity and random processes. The maximum contribution of random error is estimated and a critical value (w) determined. If the difference between any two pairs of means is less than the critical value, then the set of positions or specimens is considered homogeneous. In practice, the " best" difference is between the maximum and the minimum. If we call this value T, then if T is less than or equal to w, the set is considered homogeneous at the selected level of confidence (usually 95 % or 99 %). If T is greater than w, then the set is considered heterogeneous.

6.2 *Multiple Determinations*—The reason for taking multiple determinations on each P/S is to obtain a gage of the variation associated with the measurement process and the material being tested.

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

6.3 *Randomized Testing*—Randomizing the measurement sequences randomizes any systematic error(s) not accounted for with instrument, process, and drift controls.

NOTE 2—It is possible to extend this to any population that can be put in this form. This means that this technique can be applied to lab data generated by an interlaboratory study. Currently, interlaboratory studies, even with the aid of h and k statistics (Practice E1601), only allow the administrator to request corrections or perhaps eliminate certain data based on judgement calls. The application of this approach would allow the option of systematic elimination through the use of an accepted statistical method.

7. Lot or Batch Forms

7.1 Lots or batches may be cast or wrought.

7.1.1 A cast material lot is generally presented in the form of ingot(s) or linked pieces.

7.1.2 A wrought material lot is generally presented in the form of bar stock.

7.2 Lots or batches may be contiguous, piecewise, or a combination.

7.2.1 A contiguous lot might be a single ingot or bar.

7.2.2 A piecewise lot might be a set of pieces having been cut from bar(s), ingot(s), or linked piece casting(s). In this last case, even if the pieces have not been separated, it can be considered a piecewise lot since they are already defined.

7.2.3 A combined lot would be a set of contiguous portions such as a set of bars from a single heat.

7.3 Regardless of shape, individual specimens must be dimensionally compatible with common analytical methods.

7.3.1 Most solid form techniques require a specimen to have at least one flat analytical face.

7.3.2 If the shape of a specimen is too irregular, it will be too difficult to "clamp" to Spark-AES spark stand.

7.3.3 The preferred form is cylindrical, but any form that satisfies the above criteria is acceptable.

7.3.4 Typical forms are round, elliptical, rectangular, or hexagonal disks, truncated cones, etc.

7.3.5 Spark-AES requires a specimen to be at least 6 mm thick to minimize heating effects.

NOTE 3—When considering the use of cast material, the analyst must consider the possibility that microscopic cast structures may cause problems with the measurement technique. It is best to use a casting technique that will produce "well behaved" specimens such as chill casting.

8. The Sampling Model

8.1 *General*—The proposed sampling system is based on cylindrical geometry. That is, most lots or batches tested present themselves in some variant of cylindrical geometry. Round bar stock is fairly obvious. But even square, rectangular, hexagonal, or other such geometries work under this approach.

8.1.1 Consider the cylinder displayed in Fig. 1. The cylinder is sitting on a flat plane. For convenience, suppose the plane

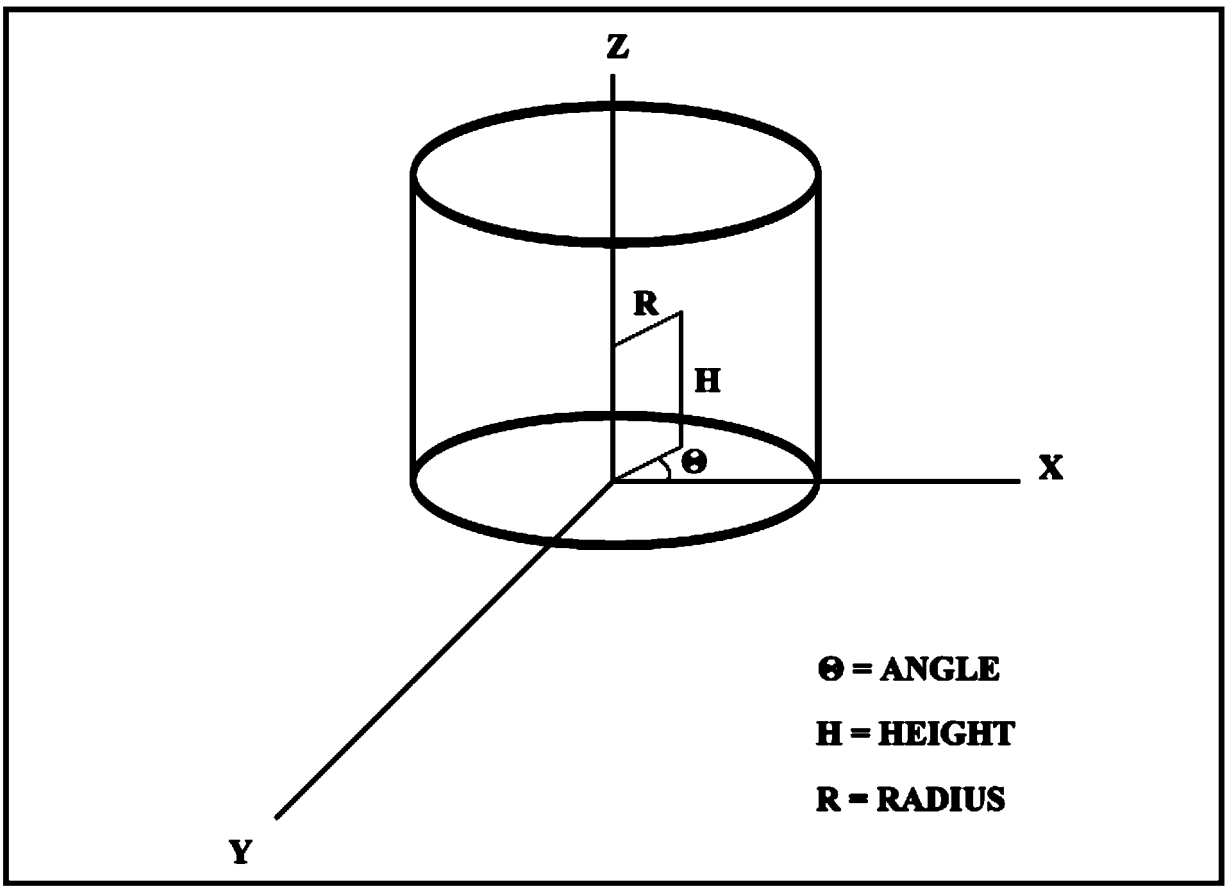

FIG. 1