ASTM INTERNATIONAL

Designation: E826 – 08

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

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[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 May 1, 2008. Published June 2008. Originally approved in 1981. Last previous edition approved in 1996 as E826 – 81 (1996) $^{\varepsilon 1}$, which was withdrawn April 2004 and reinstated in May 2008. DOI: 10.1520/E0826-08.

[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.

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

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:

$$x_{ij} = \mu + \beta_i + \tau_j + \epsilon_{ij} \qquad (1)$$

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.

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
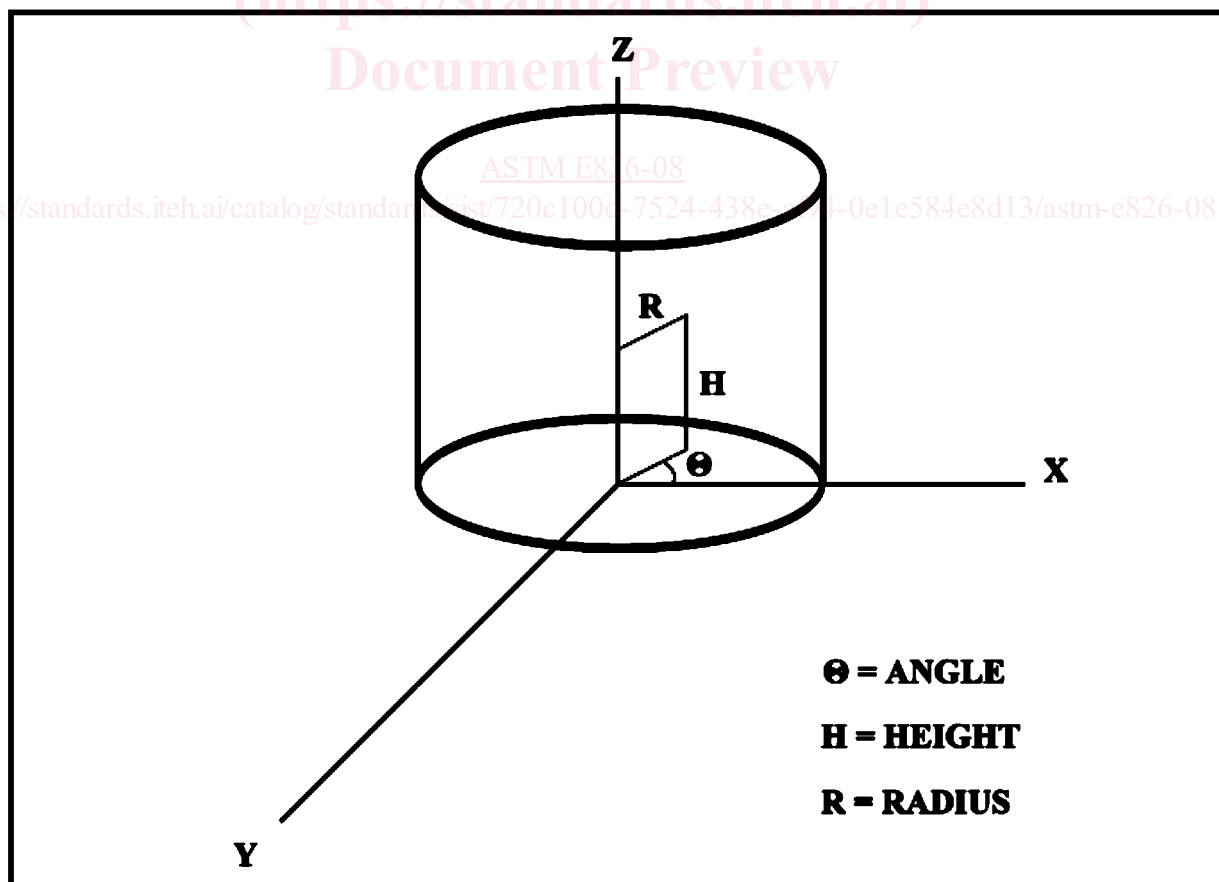

FIG. 1

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corresponds to zero height. Further, suppose the axis of the cylinder defines the origin of an XYZ coordinate system. The z axis corresponds to the cylinder axis. The x and y axes can be oriented as one chooses. Let the x axis correspond to an angle of zero degrees. Then, every point in the cylinder can be described by its height from the plane $(H \geq Z)$, its distance from the central axis (R), and its angle with respect to the x axis (Θ).

8.1.2 Given the cylindrical geometry described in 8.1.1 (Fig. 1), homogeneity can be defined in axial, radial, and circumferential terms. Axial homogeneity refers to the uniformity of the material from one end to another. Radial homogeneity refers to the uniformity of the material from the center outward. Circumferential homogeneity refers to the uniformity of the material around a concentric circle.

8.1.3 At any level (Z) the latter two are measured by selecting a number of positions on the analytical face of each sample to be so characterized. The number and position of each is a rationalization between the size and shape of the analytical face and the size of Spark-AES burn spot. A sufficient number of spots are chosen to represent a reasonable sampling of the surface.

8.1.4 Two common forms encountered are demonstrated in Figs. 2 and 3. A rationalization of sample size versus spot size dictates a seven-position strategy for round samples in the range of 25 mm to 50 mm in diameter and a nine-position strategy for square samples in the range of 25 mm to 50 mm across. For the round geometry, circumferential homogeneity is covered with Positions 1–6. Comparisons of these to Position 7 covers radial homogeneity. For the square geometry, circumferential homogeneity is covered with Positions 1–8. Comparisons of these to Position 9 covers radial homogeneity.

8.1.5 Each position is sampled four times. The positions are sequenced randomly. A typical sequence would be $a_1, a_2, \ldots a_i,$ $\ldots a_n$ where a_i is the ith randomly chosen position and n is the
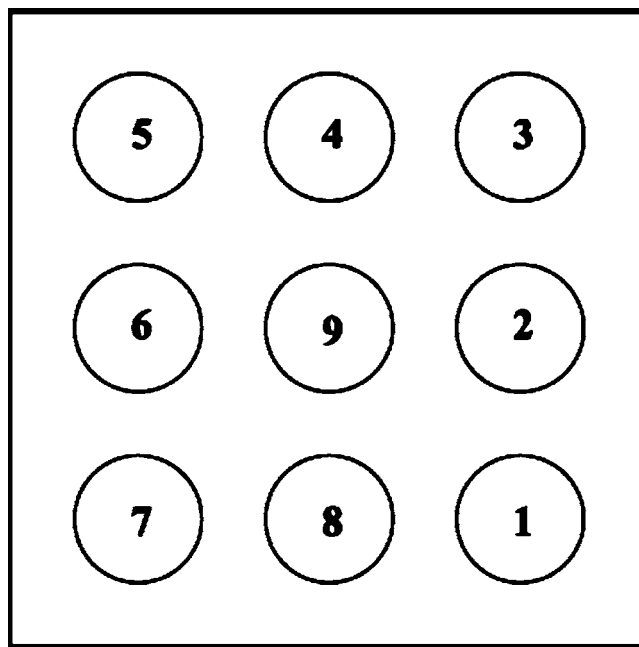

FIG. 3

total number of positions. Four such sequences are run. The resultant data are derandomized and presented as a $4 \times n$ matrix. The resultant matrix is processed in accordance with Section 12.

8.1.6 If this process is applied at any level (Z), then the entire solid can be characterized.

8.2 *Within-Unit Homogeneity (R, Θ)*—For alloys known or suspected of being heterogeneous across the face of a disk, perhaps due to migration of certain elements during cooling of castings, the analyst may need to test for homogeneity using a mapping technique. On the proposed analytical face of a selected specimen, use a mapping such as that shown in Fig. 2 or Fig. 3. Since surface preparation is a typical part of Spark-AES standard test methods, prepare the analytical face with a fresh surface produced by the normal means used by the analyst. Burn each position in random order until all are burned. Resurface and repeat with a new random burn sequence. Repeat until four sequences have been completed.

8.3 *Within-Unit Homogeneity (Z)*—For alloys known or suspected to be heterogeneous as a function of depth, it may be necessary to slice each piece at one or more distances from the original face to create test portions for (R, Θ) testing. An alternative would be to measure both faces of each piece (where practical). Another alternative would be to remove successive layers of material and test each layer so produced. This sub-sampling should be designed to allow the analyst to make a statement about the depth to which the material is to be certified for use.

8.4 *Between-Unit Homogeneity (Contiguous)*—This case occurs for ingots or bar stock. It is assumed that enough samples have been processed or enough is known about the production method so as to assure the analyst that the ingot or bar is homogeneous with respect to (R, Θ). Procure specimens representative of both ends and the middle. For each of the end
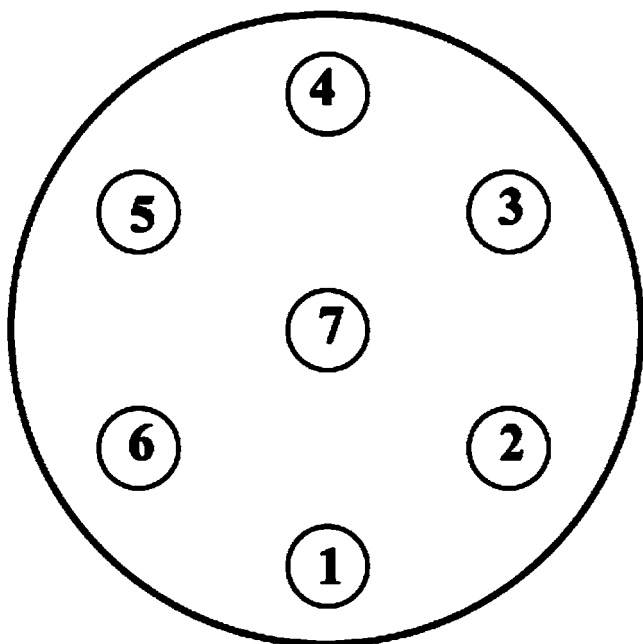

FIG. 2

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pieces use the inside face for analysis. For the middle piece either face will suffice. Surface all pieces in the normal manner. Burn each piece in random order. Burn a new random sequence. Repeat until four sequences have been burned. The resultant data are derandomized and presented as a 4 × 3 matrix. The resultant matrix is processed in accordance with Section 12.

8.5 *Between-Unit Homogeneity (Piecewise)*—This case occurs for linked-piece castings or lots where the material has already been cut into final size pieces. It is assumed that enough samples have been processed to assure the analyst that the individual pieces are homogeneous with respect to (*R*, Θ, *Z*). Select pieces in accordance with Section 10. Surface all pieces in the normal manner. Burn each piece in random order. Burn a new random sequence. Repeat until four sequences have been burned. The resultant data are derandomized and presented as a 4 × n matrix. The resultant matrix is processed in accordance with Section 12.

8.6 *Between-Unit Homogeneity (Combination)*—This case occurs when a lot is composed of more than one bar (or ingot). Label the bars with the letters A to .... For each bar procure three pieces as in 8.4. Process all pieces as in 8.4. The resultant data are derandomized and presented as a 4 × 3n matrix. The resultant matrix is processed in accordance with Section 12.

NOTE 4—The ANOVA technique used in this practice requires sufficient information about variance caused by positional and instrument variation to allow effective characterization of the effect of homogeneity on the process. For four burns at each position, the uncertainty of the standard deviation for the mean is reduced by a factor of two $\left(\sqrt{4}\right)$. The uncertainty is always reduced by the square root of the number of determinations. Nine would be better and 16 better still. However, four is a more practical number and does produce satisfactory statistics.

8.7 Specimens subject to within-unit homogeneity testing are to be chosen from the set generated in Section 10. Depending on the analysts knowledge of the L/B, all or just a strategic subset may be used. It may be necessary to take into consideration the possible effects of within-unit variation when selecting the master set (see 10.9).

9. The Test Portion

9.1 The issue of test portion size is handled differently in Spark-AES work as compared to other measurement disciplines. For example, an analyst performing a gravimetric determination of silicon (Si) would begin with a test portion of 1 gram. The final determination would be expressed as the ratio of the measured Si content to the original test portion. In Spark-AES, the determination is based on the ratio of the intensity found at the analyte line to that found at a reference line.

9.2 The quantity of material taken for each test portion is chosen to represent the smallest quantity required for a single test run according to any applicable standard test method or in-house test method applied to the matrix under examination. The purpose is to characterize the homogeneity of the reference material for the smallest practical test portion. Since Spark-AES uses a dynamic ratio technique, the test portion can be expected to scale itself to whatever excitation form or condi-

tion is used. That is, an exact knowledge of the test portion size is unnecessary because the test portion is part of the ratio process.

NOTE 5—ISO Guide 35 describes the within-bottle homogeneity test as a means to identify the minimum sample quantity representative of the entire batch of material within the capability of the test method to determine that quantity. The homogeneity test is carried out using smaller quantities of material until the standard deviation of the test portion equals the repeatability standard deviation of the test method. The analyst has the choice of which approach to use. The certificate of analysis must list either the smallest practical quantity tested for homogeneity or the largest quantity for which the standard deviation of the test portion equals the repeatability standard deviation of the test method.

9.3 Clearly, the methodology cited in 9.2 must be subjected to certain limits. Depending on the metallurgical history of a specimen, the point at which local heterogeneity will be measurable must be considered. It can be expected that specimens produced by most cast or wrought processes will appear heterogeneous at some level. The objective must be to select materials produced by methods that assure the analyst that that level is well below the size of the actual test portion. Then the assumptions of 9.2 will apply for a wide range of excitation forms and conditions.

NOTE 6—It is common practice in atomic emission methods to report the average measured signal from a number of measured portions of material. For example, four burns may be averaged and designated as a single measurement. In that case, the test portion is the total mass of sputtered material from four burns. This fact should be documented in the report.

10. Selection of Test Specimens

10.1 Practices E634, E716, and E1806 are currently the only standards that provide procedures for sampling metals. As such, they only apply to aluminum, iron, and zinc alloys. However, the analyst may use them as guidelines for sampling other metal alloys.

10.2 The sampling scheme used to pick the specimens can be random, stratified random, or in some cases systematic (ISO Guide 35). The choice depends on how the L/B was prepared and packaged.

10.3 If the candidate L/B consists of 15 or fewer specimens, then all specimens shall be tested.

10.4 If the candidate L/B is in a form or quantity that prohibits testing all specimens, then a minimum of 8 % but not less than 15 specimens shall be tested.

10.5 Generally, a maximum of 35 specimens is sufficient to represent a L/B consisting of a large number of units for which it is impractical to test 8 % of the units. In such a case, a stratified random or systematic sampling may be used.

10.6 A completely random selection of specimens can be accomplished by labeling all specimens consecutively (that is, 01, 02, 03, ...) and using a table of random numbers to select individual specimens. From a table of random numbers (**3**) (see Table 1 and Note 7), pick an arbitrary starting place and select any direction for reading the numbers, provided the direction is fixed in advance and is independent of the numbers occurring. As an alternative, a computer generated list can be used such as would be found in a random number generator (spreadsheet based or otherwise).

TABLE 1 Short Table of Random Numbers[A]

46	96	85	77	27	92	86	26	45	21	89	91	71	42	64	64	58	22	75	81	74	91	48	46	18
44	19	15	32	63	55	87	77	33	29	45	00	31	34	84	05	72	90	44	27	78	22	07	62	17
34	39	80	62	24	33	81	67	28	11	34	79	26	35	34	23	09	94	00	80	55	31	63	27	91
74	97	80	30	65	07	71	30	01	84	47	45	89	70	74	13	04	90	51	27	61	34	63	87	44
22	14	61	60	86	38	33	71	13	33	72	08	16	13	50	56	48	51	29	48	30	93	45	66	29
40	03	96	40	03	47	24	60	09	21	21	18	00	05	86	52	85	40	73	73	57	68	36	33	91
52	33	76	44	56	15	47	75	78	73	78	19	87	06	98	47	48	02	62	03	42	05	32	55	02
37	59	20	40	93	17	82	24	19	90	80	87	32	74	59	84	24	49	79	17	23	75	83	42	00
11	02	55	57	48	84	74	36	22	67	19	20	15	92	53	37	13	75	54	89	56	73	23	39	07
10	33	79	26	34	54	71	33	89	74	68	48	23	17	49	18	81	05	52	85	70	05	73	11	17
67	59	28	25	47	89	11	65	65	20	42	23	96	41	64	20	30	89	87	64	37	93	36	96	35
93	50	75	20	09	18	54	34	68	02	54	87	23	05	43	36	98	29	97	93	87	08	30	92	98
24	43	23	72	80	64	34	27	23	46	15	36	10	63	21	59	69	76	02	62	31	62	47	60	34
39	91	63	18	38	27	10	78	88	84	42	32	00	97	92	00	04	94	50	05	75	82	70	80	35
74	62	19	67	54	18	28	92	33	69	98	96	74	35	72	11	68	25	08	95	31	79	11	79	54
91	03	35	60	81	16	61	97	25	14	78	21	22	05	25	47	26	37	80	39	19	06	41	02	00
42	57	66	76	72	91	03	63	48	46	44	01	33	53	62	28	80	59	55	05	02	16	13	17	54
06	36	63	06	15	03	72	38	01	58	25	37	66	48	56	19	56	41	29	28	76	49	74	39	50
92	70	96	70	89	80	87	14	25	49	25	94	62	78	26	15	41	39	48	75	64	69	61	06	38
91	08	88	53	52	13	04	82	23	00	26	36	47	44	04	08	84	80	07	44	76	51	52	41	59
68	85	97	74	47	53	90	05	90	84	87	48	25	01	11	05	45	11	43	15	60	40	31	84	59
59	54	13	09	13	80	42	29	63	03	24	64	12	43	28	10	01	65	62	07	79	83	05	59	61
39	18	32	69	33	46	58	19	34	03	59	28	97	31	02	65	47	47	70	39	74	17	30	22	65
67	43	31	09	12	60	19	57	63	78	11	80	10	97	15	70	04	89	81	78	54	84	87	83	42
61	75	37	19	56	90	75	39	03	56	49	92	72	95	27	52	87	47	12	52	54	62	43	23	13
78	10	91	11	00	63	19	63	74	58	69	03	51	38	60	36	53	56	77	06	69	03	89	91	24
93	23	71	58	09	78	08	03	07	71	79	32	25	19	61	04	40	33	12	06	78	91	97	88	95
37	55	48	82	63	89	92	59	14	72	19	17	22	51	90	20	03	64	96	60	48	01	95	44	84
62	13	11	71	17	23	29	25	13	85	33	35	07	69	25	68	57	92	57	11	84	44	01	33	66
29	89	97	47	03	13	20	86	22	45	59	98	64	53	89	64	94	81	55	87	73	81	58	46	42
16	94	85	82	89	07	17	30	29	89	89	80	98	36	25	36	53	02	49	14	34	03	52	09	20
04	93	10	59	75	12	98	84	60	93	48	16	87	60	11	50	46	56	58	45	88	72	50	46	11
95	71	43	68	97	18	85	17	13	08	00	50	77	50	46	92	45	26	97	21	48	22	23	08	32
86	05	39	14	35	48	68	18	36	57	09	62	40	23	87	08	74	79	91	08	27	12	43	32	03
59	30	60	10	41	31	00	69	63	77	01	89	94	60	19	02	70	88	72	33	38	88	20	60	86
05	45	35	40	54	03	98	96	76	27	77	84	80	08	64	60	44	34	54	24	85	20	85	77	32
71	85	17	74	66	27	19	55	56	51	52	83	14	55	31	99	73	23	40	07	10	38	22	52	42
80	20	32	80	98	00	40	92	57	51	52	83	14	55	31	99	73	23	40	07	64	54	44	99	21
13	50	78	02	73	39	66	82	01	28	67	51	75	66	33	97	47	58	42	44	88	09	28	58	06
67	92	65	41	45	36	77	96	46	21	14	39	56	36	70	15	74	43	62	69	82	30	77	28	77
72	56	73	44	26	04	62	81	15	35	79	26	99	57	28	22	25	94	80	62	95	48	98	23	86
28	86	85	64	94	11	58	78	45	36	34	45	91	38	51	10	68	36	87	81	16	77	30	19	36
69	57	40	80	44	94	60	82	94	93	98	01	48	50	57	69	60	77	69	60	74	22	05	77	17
71	20	03	30	79	25	74	17	78	34	54	45	04	77	42	59	75	78	64	99	37	03	18	03	36
89	98	55	98	22	45	12	49	82	71	57	33	28	69	50	59	15	09	25	79	39	42	84	18	70
58	74	82	81	14	02	01	05	77	94	65	57	70	39	42	38	48	56	84	31	13	18	70	41	60
50	54	73	81	91	07	81	26	25	45	49	61	22	88	41	20	00	15	59	93	51	60	65	65	63
49	33	72	90	10	20	65	28	44	63	95	86	75	78	69	24	41	65	86	10	34	10	32	00	93
11	85	01	43	65	02	85	69	56	88	34	29	64	35	48	15	70	11	77	83	01	34	82	91	04
34	22	46	41	84	74	27	02	57	77	47	93	72	02	95	63	75	74	69	69	61	34	31	92	13

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10.7 Select those specimens for testing that match the numbers read from the table or list.

NOTE 7—Table 1 included herein is for example, only. Use the more complete tables in Ref (**3**) when actually using this test procedure. In the alternative approach, if a spreadsheet is used, use the random number function(s) to generate the selected subset.

NOTE 8—Since many metal L/B candidates come from bars, they should be tested before they are cut up. Random sampling of the cut pieces can miss or mask systematic inhomogeneity.

10.8 Because batches of chemical reference materials typically consist of hundreds or even thousands of units, stratified random sampling is used to ensure that the selected specimens represent the entire preparation and packaging sequence (**4**). The population may be divided into groups as a consequence of the preparation or manufacture of the material, or it may be divided by the analyst into n equal-sized groups corresponding to the sequential order of preparation (for example, bars

formed or castings poured). One or more units are selected at random from each group.

10.9 A systematic choice of specimens may be made if circumstances warrant. For example, the condition of one or more molds may affect the composition of a cast lot due to improper teaming behavior. In such a case, the analyst may choose to include the first unit and several additional units in the homogeneity test. Systematic selection of a small number of units should be done prior to the application of random or stratified random sampling.

11. Test Procedure

11.1 It is necessary to perform the homogeneity testing in two steps. The first is the within-unit step. The second is the between-unit step.

11.2 Select optimum instrumental conditions to obtain adequate sensitivity for each element to be tested in the specimens. Use excitation conditions appropriate for the element(s) of interest.

11.3 For each element of interest, select a spectral line that has minimal interferences from other elements in the specimen.

11.4 Measure the element(s) of interest in each specimen selected in Section 10. For each specimen, the positions shall be taken in random order. After all positions have been burned for a particular specimen, resurface it and repeat the process. Repeat the burn sequences until enough burns have been performed for each position to allow the production of "good" statistics. Generally, four burns for each position will suffice.

NOTE 9—The concept of good here is related to the inherent uncertainty in the standard deviation. This is known to vary as the square root of the number of determinations. Four burns halves it. Nine reduces it to a third. Sixteen reduces it to a fourth, and so on. Practicality suggests limiting the number to a compromise between the need for precision and the expense of performing the test.

11.5 Enter the data from 11.4 for each specimen into Table 2 and process it according to the method given in Section 12.

11.6 If all the specimens tested for within-unit homogeneity are found to be unsatisfactory, the process should be stopped, the L/B declared nonhomogeneous, and marked accordingly. They are not to be considered suitable for the intended use.

NOTE 10—If the need for the lot is sufficiently great or time sensitive, it may be possible to proceed anyway provided the end user is notified and an effort to characterize the heterogeneity is made. A follow up study would be able to determine how much uncertainty to assign to this source of error.

11.7 If some of the specimens tested for within-unit homogeneity fail but the rest pass, a suitable subset may be selected that will be usable.

11.8 If all the specimens tested for within-unit homogeneity pass, the full set in Section 10 may be processed for between-unit (L/B) homogeneity testing.

11.9 Measure the element(s) of interest in the specimens selected in Section 10. For each set, the specimens shall be taken in random order. After all specimens have been burned, start a new burn sequence. Repeat the burn sequences until enough burns have been performed for each specimen to allow the production of "good" statistics (see Note 9). Generally, four burns for each specimen will suffice.

11.10 Enter the data from 11.9 for the set into Table 2 and process it according to the method given in Section 12.

11.11 If some of the specimens tested for between-unit homogeneity fail but the rest pass, a suitable subset may be selected that will be usable.

NOTE 11—Sometimes it happens that a L/B can be split into two or more homogeneous subsets. See Appendix X3 for an example.

11.12 If all the specimens tested for between-unit homogeneity pass, the full set in Section 10 may be applied to its intended purpose.

11.13 Since Spark-AES units are known to drift over a large number of determinations, drift correction is almost certain to be required. One or more drift monitors should be used as standard practice.

NOTE 12—It has been suggested that control samples could be used here and that as long as they stayed within "known" control limits that no drift correction would be needed. Still, drift is drift and if it can be detected, it should be corrected for. The test of 13.1 would be a better guide.

11.13.1 For within-unit testing, monitor(s) should be run after every two to four candidate burns. A particular burn sequence for a 32-mm round specimen might look like this: M, 3, 5, 2, 7, M, 4, 1, 6, M—for a single monitor (M) drift correction routine.

NOTE 13—The rational for choosing this frequency range is based on a compromise between sample size, burn spot size, and measurement efficacy. Most applications involve samples in the range of 32 mm to 50 mm. This is because most testing is done using Spark-AES or XRF. Many laboratories do both. The latter requires test pieces to be in the cited size range. Typical spot size for Spark-AES burn is approximately 6 mm. R, Θ within-unit homogeneity for such a sample size limits spot placement to around seven to nine distinct locations (see Figs. 2 and 3). For each run, the monitor(s) must be run often enough to assure the analyst that a "true" picture of drift is obtained. Too few determinations might give too much weight to any one monitor determination. Too many determinations would require unnecessary work. The cited case only requires three monitor determinations.

11.13.2 For between-unit testing, monitor(s) should be run after every four to ten candidate burns. A particular burn sequence for 15 specimens might look like this: L, H, 13, 5, 7, 2, L, 4, 11, 6, 15, H, 1, 14, 8, 3, L, 9, 12, 10, L, H—for a double monitor (L, H) drift correction routine.

NOTE 14—The limitations of sample size versus spot size go away in this case as the ability to place four distinct burns on a sample is reasonably assured. This leaves only the issue of measurement efficacy. The analyst is expected to have a reasonable knowledge of the drift characteristics of an instrument. The selection of monitor frequency is a rationalization between available time and resources and the need for an adequate picture of the drift patterns for the various runs.

TABLE 2 The Homogeneity Testing ANOVA

Position or Specimen	Burn Number						T	T^2	X^2	t'
	1	2	3	4	...	b				
1	x_{11}	x_{12}	x_{13}	x_{14}	...	x_{1b}	$T_1 = \Sigma\, x_{1j}$	T_1^2	$X_1^2 = \Sigma\, x_{1j}^2$	$t_1 = T_1/b$
2	x_{21}	x_{22}	x_{23}	x_{24}	...	x_{2b}	$T_2 = \Sigma\, x_{2j}$	T_2^2	$X_2^2 = \Sigma\, x_{2j}^2$	$t_2 = T_2/b$
3	x_{31}	x_{32}	x_{33}	x_{34}	...	x_{3b}	$T_3 = \Sigma\, x_{3j}$	T_3^2	$X_3^2 = \Sigma\, x_{3j}^2$	$t_3 = T_3/b$
.	.	.	.	.	...	.	.	.	.	.
.	.	.	.	.	...	.	.	.	.	.
.	.	.	.	.	...	.	.	.	.	.
t	x_{t1}	x_{t2}	x_{t3}	x_{t4}	...	x_{tb}	$T_t = \Sigma\, x_{tj}$	T_t^2	$X_t^2 = \Sigma\, x_{tj}^2$	$t_t = T_t/b$
B	$B_1 = \Sigma\, x_{i1}$	$B_2 = \Sigma\, x_{i2}$	$B_3 = \Sigma\, x_{i3}$	$B_4 = \Sigma\, x_{i4}$	...	$B_b = \Sigma x_{ib}$			$G = \Sigma T_j$	
B^2	B_1^2	B_2^2	B_3^2	B_4^2	...	$B_{b^1}^2$				

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11.14 Examine the data and discard any values that have been determined to be outliers according to Practice E178. If any outliers occur, repeat the complete test, as provision is not made for missing data in the mathematical treatment.

NOTE 15—If an outlier condition is detected or suspected, the P/S producing it should be examined for possible cause. Was an inclusion encountered? Was it just a wild burn? Answering these questions may preclude the need for substantial additional work.

NOTE 16—If the cause is material based, it may lead to the discovery of a more general problem with the L/B.

NOTE 17—If the cause is burn related, it may be possible to repeat only a portion of the whole test. For example, if only one run is effected, it may be possible to substitute another for it. See Note 40 for a strategy that may allow this.

12. Calculations to Determine Homogeneity

12.1 Perform a one-way analysis of variance on the within-unit data for selected specimens using a computerized, spreadsheet program. Perform a one-way analysis of variance on the between-unit data for selected specimens using a computerized, spreadsheet program. If needed, perform a one-way analysis of variance on the depth study data for selected specimen(s) using a computerized, spreadsheet program. In each case, the program must calculate and tabulate the following quantities indicated in Table 2 and steps 12.2 through 12.10.

NOTE 18—This study should be as limited as the data and the confidence of the analyst allows as it is totally destructive.

NOTE 19—For most cases, the tabular and reported quantities will be in concentration percent. However, there is no such limitation on the application of the practice itself. Units may be percent, parts-per-million, or any other suitable unit. The reported quantities (t_j', s, w, etc.) will be in the same units as the tabular entries (x_{11}, x_{12}, etc.). The squared units (T_j^2, B_i^2, Sst, etc.) will be in the square of the units of the tabular entries.

12.2 Compute T_j, T_j^2, B_i, B_i^2, X_j^2, t_j', and G, (see Table 2), where: T_j = the sum of row j; B_i = the sum of column i; X_j^2 = the sum of the squares of row j, t_j' = the mean of row j; and G = the sum of T_j; b = number of burns per P/S; and t = number of P/S.

12.3 Choose a significance level (α) for the test.

NOTE 20—A 5 % significance level is recommended for this procedure. See Ref (2) for more extensive tables containing values at other significance levels.

12.4 From Table 3, obtain the q value that corresponds to t and n, where: n = the number of degrees of freedom:

$$n = (b - 1)(t - 1) \quad (2)$$

12.5 Compute SSt = sum of squares due to P/S:

$$SSt = \left[(T_1^2 + T_2^2 + \dots T_t^2)/b\right] - (G^2/tb) = \left[\sum T_j^2/b\right] - (G^2/tb) \quad (3)$$

12.6 Compute SSb = sum of squares due to burns:

$$SSb = \left[(B_1^2 + B_2^2 + \dots B_b^2)/t\right] - (G^2/tb) = \left[\sum B_i^2/t\right] - (G^2/tb) \quad (4)$$

12.7 Compute SST = sum of the squares of all the measurements in the ANOVA and subtract G^2/tb:

$$SST = \sum\sum x_{ij}^2 - (G^2/tb) = \sum X_j^2 - (G^2/tb) \quad (5)$$

where:

x_{ij} = individual values in the table.

NOTE 21—This is often called the total sum of squares, hence SST.

12.8 Compute:

$$s = \sqrt{\frac{(SST - SSb - SSt)}{(b - 1)(t - 1)}} \quad (6)$$

12.9 Compute:

$$w = qs/\sqrt{b} \quad (7)$$

12.10 If the absolute difference between any two mean values (that is, $t_1' \dots t_t'$) exceeds w, then there is strong evidence, at the 95 % confidence level, that the specimens are not homogeneous. If the absolute difference between any two mean values does *not* exceed w, then the specimens shall be considered homogeneous.

NOTE 22—Unindexed summations have been used throughout as it is clear from the subscripts and the contexts what the indices and limits are.

NOTE 23—The easiest way to obtain the maximum difference is to extract the largest and smallest means and take the difference between the two.

13. Drift Correction by the Interpolation Method

13.1 *Test for Instrumental Drift*—This test for drift is made on repeat analyses of the monitor (M) measured along with the specimens (5-7). The monitor is measured at the beginning of each test set, repeated at an interval no greater than every tenth specimen, and at the end of the test set.

NOTE 24—The question of the measurement form is raised here. Should the measurements be in intensities, intensity ratios, or fully corrected concentrations. Since the monitor(s) may be somewhat different from the candidate, it may be subject to different effects. It is best to use fully corrected concentrations.

13.1.1 Select the monitor frequency (such as, three, five, or ten) and maintain this measurement sequence throughout the entire test.

13.1.2 Arrange the measurements on the monitor in the exact sequence in which they were made. For example: M_1, M_2, M_3, ... , M_n, where n = the number of times the monitor is run in the sequence.

13.1.3 Obtain the differences (D_i) between immediately successive measurements as follows:

$$D_1 = M_1 - M_2; D_2 = M_2 - M_3, \dots, D_{n-1} = M_{n-1} - M_n \quad (8)$$

13.1.4 Calculate the mean square of successive difference S_1^2 as follows:

$$S_1^2 = \sum D_i^2/(n - 1) \quad (9)$$

13.1.5 Calculate the variance S_2^2 as follows:

$$S_2^2 = \sum d_i^2/(n - 1) \quad (10)$$

where:

d_i = difference between the ith measurement on the monitor (M_i) from the overall average of the measurements on the monitor $(\overline{M}) = M_i - \overline{M}$.

13.1.6 Calculate the ratio (5-7):

$$R = S_1^2/S_2^2 \quad (11)$$

13.1.6.1 If R is *larger* than the value listed in Table 4 for the number of times the monitor was measured (n), there is not sufficient evidence at the 95 % confidence level to indicate that drift has occurred. If no drift has occurred, the derandomized values obtained on the specimens should be tabulated in Table

TABLE 3 Values of *q* for Various Combinations of *t* and *n* at the 5 % Significance Level

$n\downarrow$	$t\rightarrow$	2	3	4	5	6	7	8	9	10
1		17.97	26.98	32.82	37.08	40.41	43.12	45.40	47.36	49.07
2		6.08	8.33	9.80	10.88	11.74	12.44	13.03	13.54	13.99
3		4.50	5.91	6.82	7.50	8.04	8.48	8.85	9.18	9.46
4		3.93	5.04	5.76	6.29	6.71	7.05	7.35	7.60	7.83
5		3.64	4.60	5.22	5.67	6.03	6.33	6.58	6.80	6.99
6		3.46	4.34	4.90	5.30	5.63	5.90	6.12	6.32	6.49
7		3.34	4.16	4.68	5.06	5.36	5.61	5.82	6.00	6.16
8		3.26	4.04	4.53	4.89	5.17	5.40	5.60	5.77	5.92
9		3.20	3.95	4.41	4.76	5.02	5.24	5.43	5.59	5.74
10		3.15	3.88	4.33	4.65	4.91	5.12	5.30	5.46	5.60
11		3.11	3.82	4.26	4.57	4.82	5.03	5.20	5.35	5.49
12		3.08	3.77	4.20	4.51	4.75	4.95	5.12	5.27	5.39
13		3.06	3.73	4.15	4.45	4.69	4.88	5.05	5.19	5.32
14		3.03	3.70	4.11	4.41	4.64	4.83	4.99	5.13	5.25
15		3.01	3.67	4.08	4.37	4.59	4.78	4.94	5.08	5.20
16		3.00	3.65	4.05	4.33	4.56	4.74	4.90	5.03	5.15
17		2.98	3.63	4.02	4.30	4.52	4.70	4.86	4.99	5.11
18		2.97	3.61	4.00	4.28	4.49	4.67	4.82	4.96	5.07
19		2.96	3.59	3.98	4.25	4.47	4.65	4.79	4.92	5.04
20		2.95	3.58	3.96	4.23	4.45	4.62	4.77	4.90	5.01
24		2.92	3.53	3.90	4.17	4.37	4.54	4.68	4.81	4.92
30		2.89	3.49	3.85	4.10	4.30	4.46	4.60	4.72	4.82
40		2.86	3.44	3.79	4.04	4.23	4.39	4.52	4.63	4.73
60		2.83	3.40	3.74	3.98	4.16	4.31	4.44	4.55	4.65
120		2.80	3.36	3.68	3.92	4.10	4.24	4.36	4.47	4.56
∞		2.77	3.31	3.63	3.86	4.03	4.17	4.29	4.39	4.47

$n\downarrow$	$t\rightarrow$	11	12	13	14	15	16	17	18	19	20
1		50.59	51.96	53.20	54.33	55.36	56.32	57.22	58.04	58.83	59.56
2		14.39	14.75	15.08	15.38	15.65	15.91	16.14	16.37	16.57	16.77
3		9.72	9.95	10.15	10.35	10.52	10.69	10.84	10.98	11.11	11.24
4		8.03	8.21	8.37	8.52	8.66	8.79	8.91	9.03	9.13	8.23
5		7.17	7.32	7.47	7.60	7.72	7.83	7.93	8.03	8.12	8.21
6		6.65	6.79	6.92	7.03	7.14	7.24	7.34	7.43	7.51	7.59
7		6.30	6.43	6.55	6.66	6.76	6.85	6.94	7.02	7.10	7.17
8		6.05	6.18	6.29	6.39	6.48	6.57	6.65	6.73	6.80	6.87
9		5.87	5.98	6.09	6.19	6.28	6.36	6.44	6.51	6.58	6.64
10		5.72	5.83	5.93	6.03	6.11	6.19	6.27	6.34	6.40	6.47
11		5.61	5.71	5.81	5.90	5.98	6.06	6.13	6.20	6.27	6.33
12		5.51	5.61	5.71	5.80	5.88	5.95	6.02	6.09	6.15	6.21
13		5.43	5.53	5.63	5.71	5.79	5.86	5.93	5.99	6.05	6.11
14		5.36	5.46	5.55	5.64	5.71	5.79	5.85	5.91	5.97	6.03
15		5.31	5.40	5.49	5.57	5.65	5.72	5.78	5.85	5.90	5.96
16		5.26	5.35	5.44	5.52	5.59	5.66	5.73	5.79	5.84	5.90
17		5.21	5.31	5.39	5.47	5.54	5.61	5.67	5.73	5.79	5.84
18		5.17	5.27	5.35	5.43	5.50	5.57	5.63	5.69	5.74	5.79
19		5.14	5.23	5.31	5.39	5.46	5.53	5.59	5.65	5.70	5.75
20		5.11	5.20	5.28	5.36	5.43	5.49	5.55	5.61	5.66	5.71
24		5.01	5.10	5.18	5.25	5.32	5.38	5.44	5.49	5.55	5.59
30		4.92	5.00	5.08	5.15	5.21	5.27	5.33	5.38	5.43	5.47
40		4.82	4.90	4.98	5.04	5.11	5.16	5.22	5.27	5.31	5.36
60		4.73	4.81	4.88	4.94	5.00	5.06	5.11	5.15	5.20	5.24
120		4.64	4.71	4.78	4.84	4.90	4.95	5.00	5.04	5.09	5.13
∞		4.55	4.62	4.68	4.74	4.80	4.85	4.89	4.93	4.97	5.01

2, and then the calculations to determine homogeneity performed. However, if *R* is *smaller* than the value listed in Table 4 for the n runs, then there is strong evidence, with 95 % confidence, that drift has occurred. When drift has occurred, make corrections as specified in 13.2.

13.2 *Calculation of Drift Factors*—Correct the measured values obtained on the specimens by calculating drift factors as follows:

13.2.1 Arrange the data obtained on the monitor in chronological order (M_1, M_2, M_3, ... , M_n).

13.2.2 Compute the drift factors (F_i) as follows:

$$F_1 = (M_1 + M_2)/2M_1 \qquad (12)$$

$$F_2 = (M_2 + M_3)/2M_1 \qquad (13)$$

$$F_{n-1} = (M_{n-1} + M_n)/2M_1 \qquad (14)$$

13.2.3 Divide the measured values in their original sequence by the *appropriate* drift factor to obtain corrected values, for example, observed value/F_i = corrected value (see example X1.3.5 and Table X1.2).

13.2.4 Derandomize drift-corrected values, enter in Table 2, and determine homogeneity as described in Section 12.

14. Drift Correction by the Least-Squares, Single Monitor Method

NOTE 25—The term "least-squares fit" is a common shorthand for the more correct term "least-squares regression." In this practice it is a statistical method for determining the "best" estimate of the coefficients of a polynomial. The degree or order of a polynomial is the highest power

TABLE 4 Critical Values for Determining Occurrence of Drift from the $R = S_1^2/S_2^2$ Ratio[A]

Number of Measurements (n) on Monitor	Ratio
4	0.78
5	0.82
6	0.89
7	0.94
8	0.98
9	1.02
10	1.06
11	1.10
12	1.13
15	1.21
20	1.30
25	1.37

[A] This table from (3) is shown as an example. For more complete tables, see (3 and 4). However, the values in the latter references are half the values shown in this table because of a slightly different method of determination.

monomial in the polynomial. In this section the polynomial is first-degree (linear). In subsequent sections second-degree (quadratic) or third-degree (cubic) polynomials will be considered. In a case where a first-degree polynomial fails as a satisfactory model, a second-degree polynomial is tested. If a second-degree polynomial fails as a satisfactory model, a third-degree polynomial is tested. The shorthand terminology for this process is selecting a higher degree fit. In no case will a polynomial of degree higher than third be considered or allowed.

14.1 This drift correction method (8) assumes the existence of drift throughout a testing sequence. This situation is common for Spark-AES. A typical case might be a drift monitor, one or more calibrants (see Section 17), and 15 or more specimens for homogeneity testing. Assuming five calibrants, running the drift monitor every fifth determination, and the 15 specimens, a single run will have 26 determinations. If a full testing scheme is comprised of four runs, this is a total of 104 determinations.

NOTE 26—The test of 13.1 can be applied if the analyst desires. The drift monitor should be run as if drift is expected. If the test indicates drift, then the correction is to be made so as to reduce error introduced from this source. If the test does not indicate drift, then the correction should not be made so as avoid the introduction of error from statistical variation in the measurements.

14.2 In the case cited in 14.1, there are six drift monitor determinations per run. If the unit has been properly prepared, warmed up, and determinations made in a timely manner (short breaks between), then the drift pattern will approximate a linear trend line. A least-squares fit of drift monitor values versus sequence number will produce a sequential drift equation which can be applied to other determinations in the sequence.

NOTE 27—The analyst is not limited to a linear drift pattern. Any non-linear scheme that can be fit may be used.

14.3 Since only a single drift monitor is used in this scheme, the analyst must choose whether to use an offset (intercept) or rotational (slope) sequential drift correction equation. This is because the line formed by the drift monitor sequence of values can rotate or translate. The analyst who is familiar with the characteristics of the measurement instrument will be able to determine which equation to use.

NOTE 28—It has been suggested that a solution to the problem of having to choose is to select one of the candidate samples as a drift monitor. Then, all corrections would be offset. There are two problems with this approach. The first is associated with the question of the homogeneity of

the selected sample with respect to itself and the other samples in the testing sequence. While the examples cited here are primarily between-unit, the arguments also apply to within-unit. Sample homogeneity is the question at hand! The second is associated with the ability of the analyst to be assured that the monitor and candidate samples have been run in the correct sequence. The monitor should be different enough to determine the proper placement of monitor burns.

14.4 The offset sequential drift correction equation is reasonably straightforward. For each step in the determination sequence, an incremental amount is added to compensate for drift. The increment may be positive or negative. The increment is the slope determined by the least-squares fit but of the opposite sign multiplied by the sequence number.

14.5 The rotational sequential drift correction equation is not so straightforward. The increment is now a function of both the slope and the constant. This is because the concentrations of the drift monitor and that of the specimens for every element can be expected to differ. This means the increment for the rotational sequential drift correction equation must be a ratio of the slope to the constant (drift per unit concentration) multiplied by the sequence number.

14.6 In the case cited in 14.1, for a particular element for a particular sequence, the drift monitor might produce the six values: M_1, M_6, M_{11}, M_{16}, M_{21}, and M_{26}. A least-squares fit of these versus the corresponding sequence numbers for them (1, 6, 11, 16, 12, 26) yields a constant (M_0) and an increment (I).

14.7 The equation being fit is:

$$M_i = M_0 + Ii \qquad (15)$$

where:
M_i = the ith drift monitor value,
M_0 = a constant (the drift free or initial value),
I = the drift increment per determination, and
i = the ith determination in the sequence.

14.7.1 Note that the independent variable is the determination sequence number and the dependent variable is the determined value.

14.8 For the case where an offset sequential drift correction equation is in order, the equation is:

$$V_i' = V_i - Ii \qquad (16)$$

where:
V_i' = the ith drift corrected value,
V_i = the ith uncorrected value, and
Ii = the drift correction.

14.9 For the case where a rotational sequential drift correction equation is in order, the equation is:

$$V_i' = \frac{V_i}{(1 + iI/M_0)} \qquad (17)$$

where all the terms are as cited above.

14.10 Apply the appropriate equation to the data in the sequence(s) generated, derandomize drift-corrected values, enter in Table 2, and determine homogeneity as described in Section 12.

NOTE 29—By including the M data in the sequence, a check is provided for the effectiveness of the correction scheme.

NOTE 30—If two square sums are created, $SSM = \sum (M_i - M_0)^2$ and