



Designation: E826 – 14

Standard Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectrometry¹

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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

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.

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

³ 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 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:

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

where:

x_{ij} = the result of the i th burn on the j th P/S,

μ = the "true" mean of the population of all possible burn results,

β_i = the variation in the i th burn due to the measurement process,

τ_j = the variation in the j th 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

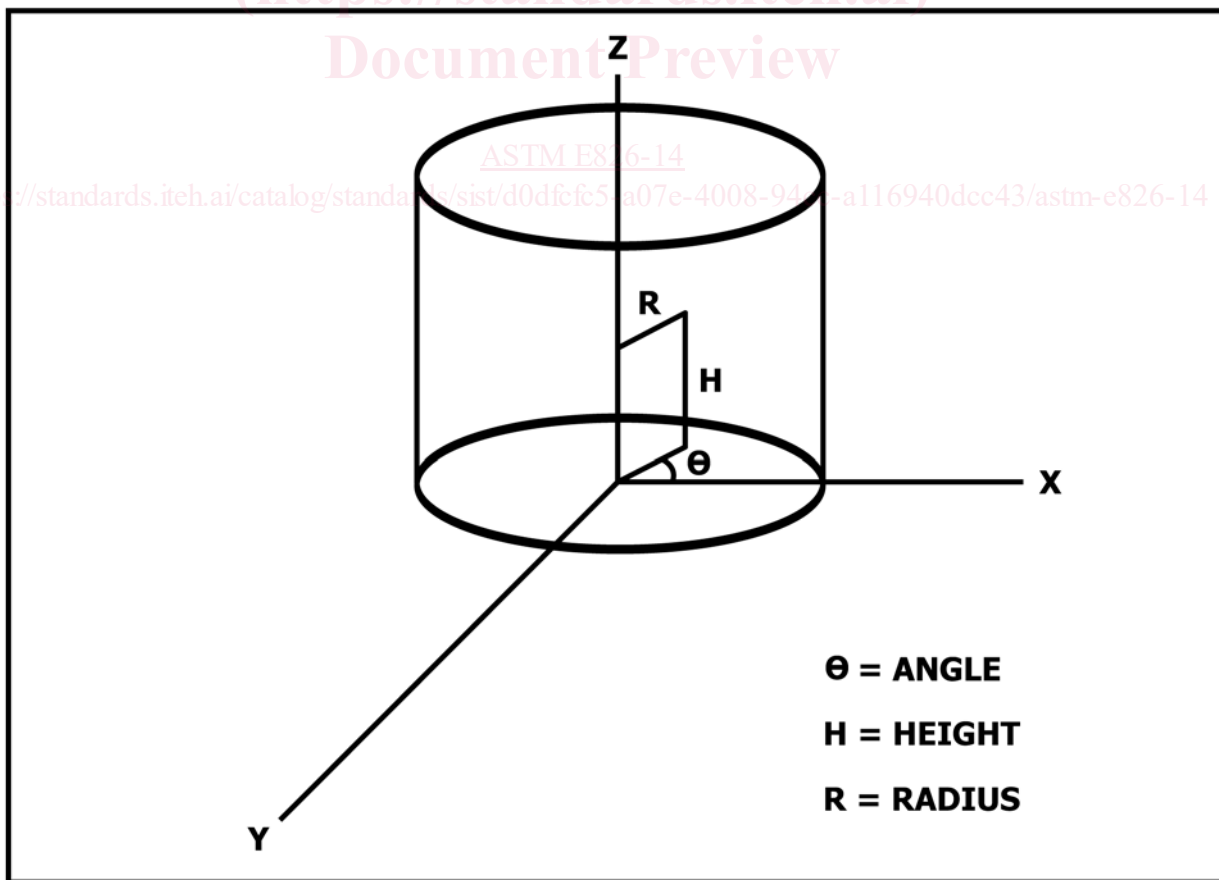


FIG. 1

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. Although the sample is resurfaced between samplings and material is removed for any one test piece, this resurfacing is not to be considered a change in Z .

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.

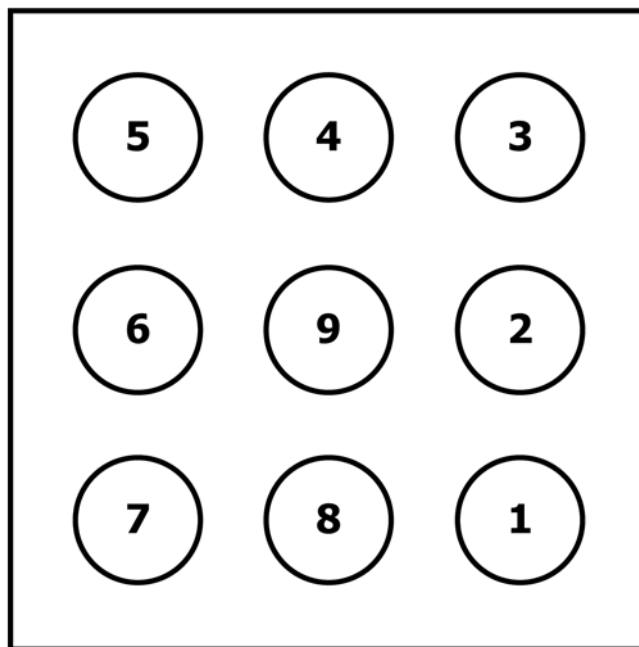


FIG. 3

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

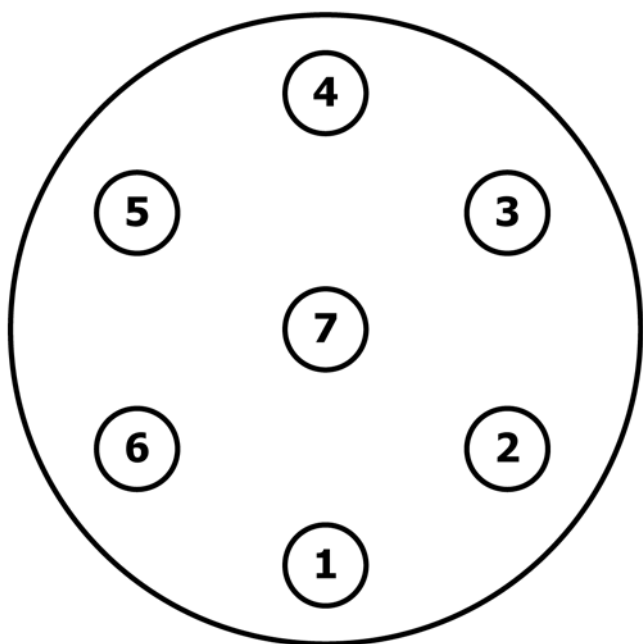


FIG. 2

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 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 $4 \times n$ 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 $4 \times 3n$ 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 ($\sqrt{4}$). 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 condition 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 fewer 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.

TABLE 1 Short Table of Random Numbers⁴

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	68	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	28	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	85	19	55	56	51	36	48	92	32	44	40	47	10	38	22	52	42	29	96
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	48	56	84	31	59	18	70	41	74	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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As an alternative, a computer generated list can be used such as would be found in a random number generator (spreadsheet based or otherwise).

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 rationale 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.

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}	$T_1 = \sum x_{1j}$	T_1^2	$X_1^2 = \sum x_{1j}^2$	$t'_1 = T_1/b$
2	x_{21}	x_{22}	x_{23}	x_{24}	...	x_{2b}	$T_2 = \sum x_{2j}$	T_2^2	$X_2^2 = \sum x_{2j}^2$	$t'_2 = T_2/b$
3	x_{31}	x_{32}	x_{33}	x_{34}	...	x_{3b}	$T_3 = \sum x_{3j}$	T_3^2	$X_3^2 = \sum x_{3j}^2$	$t'_3 = T_3/b$
...
t	x_{t1}	x_{t2}	x_{t3}	x_{t4}	...	x_{tb}	$T_t = \sum x_{tj}$	T_t^2	$X_t^2 = \sum x_{tj}^2$	$t'_t = T_t/b$
B	$B_1 = \sum x_{1j}$	$B_2 = \sum x_{2j}$	$B_3 = \sum x_{3j}$	$B_4 = \sum x_{4j}$...	$B_b = \sum x_{bj}$			$G = \sum T_j$	
B ²	B_1^2	B_2^2	B_3^2	B_4^2	...	B_b^2				

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.

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:

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

12.6 Compute SSb = sum of squares due to burns:

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

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. A finding that the material is not homogeneous using this test does not necessarily mean that the material is unusable. It is up to the user of this practice to determine the suitability of the candidate material (reference 1.3).

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:

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

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	9.23
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

where:

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

13.1.6 Calculate the ratio (5-7):

$$R = S_i^2/S^2 \quad (11)$$

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 2, and then the calculations to determine homogeneity per-

formed. 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 ($M_1, M_2, M_3, \dots, M_n$).

13.2.2 Compute the drift factors (F_i) as follows:

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

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

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.

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

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 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 to 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, 21, 26) yields a constant (M_0) and an increment (I).

14.7 The equation being fit is:

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

where:

M_i = the i th drift monitor value,
 M_0 = a constant (the drift free or initial value),
 I = the drift increment per determination, and
 i = the i th 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:

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

where:

V_i' = the i th drift corrected value,