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

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:

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

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
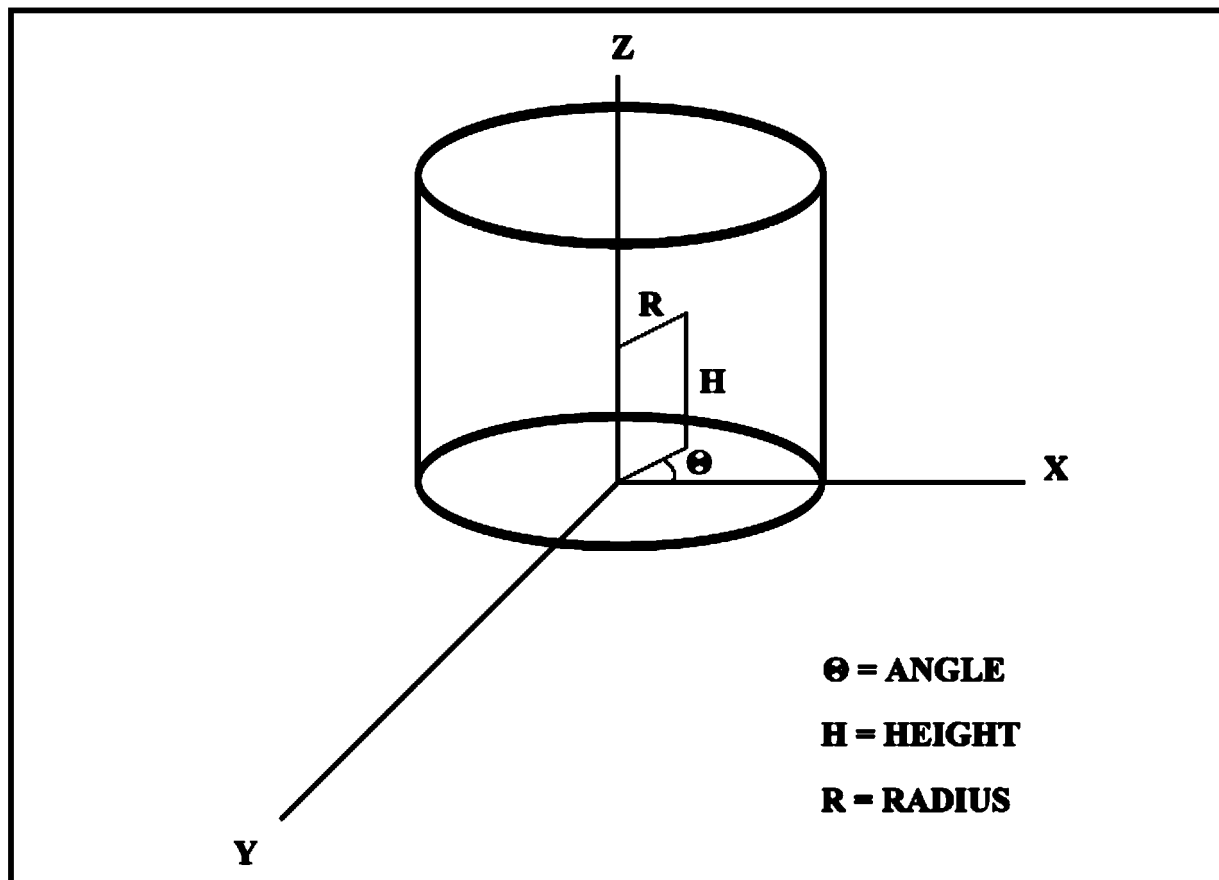

FIG. 1

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.
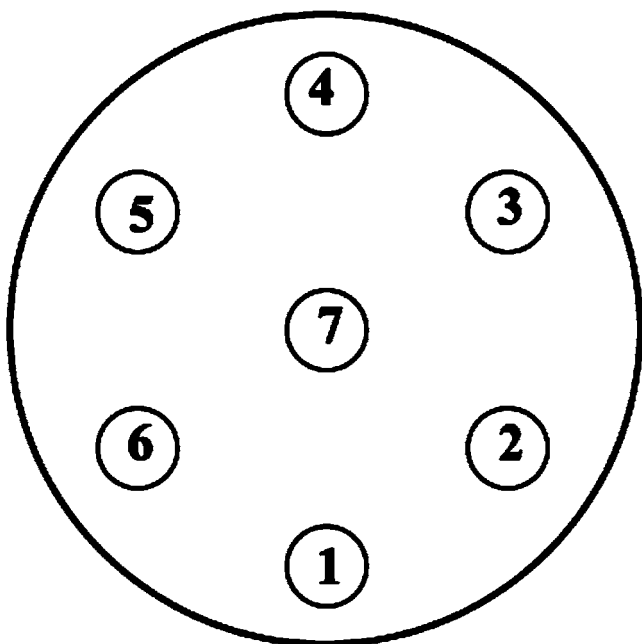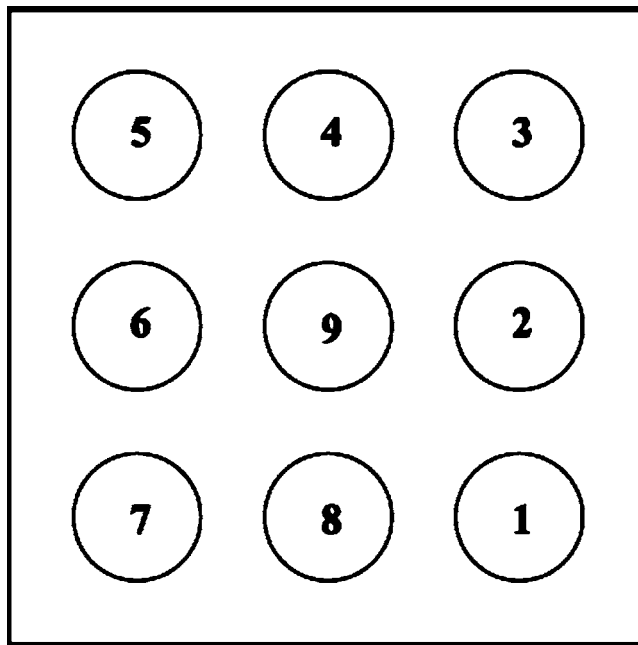
FIG. 3

8.1.5 Each position is sampled four times. The positions are sequenced randomly. A typical sequence would be $a_1, a_2, ... a_i,$ ... a_n where a_i is the ith 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 $\left(\sqrt{4} \right)$. 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 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 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	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 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.

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	...	$B_{b^1}^2$				

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:

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

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

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

12.6 Compute SSb = sum of squares due to burns:

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

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

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

where:

x_{ij} = individual values in the table.

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

12.8 Compute:

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

12.9 Compute:

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

12.10 If the absolute difference between any two mean values (that is, $t_1'\ldots t_t'$) 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:

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

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

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

13.1.5 Calculate the variance S_2^2 as follows:

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

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	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

where:

d_i = difference between the *i*th 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):

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

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, ... , M_n).

13.2.2 Compute the drift factors (F_i) as follows:

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

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

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.

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

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 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:

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

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 $SSM^{'} = \sum (M_i^{'} - M_0)^2$, then the ratio SSM'/SSM will provide useful information about the effectiveness of the correction scheme.

15. Drift Correction by the Least-Squares, Multiple Monitor Method

15.1 To fully evaluate drift behavior, it is necessary to use at least two drift monitors. Then, rotation and translation can simultaneously be accounted for. This scheme is described for only two monitors. However, it can be applied to more than two.

15.2 This method follows the reasoning that is normally applied to standardization. A high end monitor (H) is sensitive to rotational effects and a low end monitor (L) is sensitive to offset effects. If it is known how these two drift with time, then it should be known how any point between or near drifts with time. Generally, H should be greater than or equal ($\geq$) to 80 % of the measurement range of interest. Generally, L should be approximately twice the detection limit of the line for the element being measured.

15.3 It is assumed that as the burns are carried out, the changes in instrument parameters (component heating, argon flush purification, etc.) cause the readings to drift in a linear manner (see Notes 26 and 27). For such a case, the drift equation has the general form:

$$y_i = A_i x_i + a_i \quad (18)$$

where:
y_i = the drift corrected value for the ith determination,
A_i = the rotational drift factor for the ith determination,
x_i = the uncorrected value for the ith determination, and
a_i = the offset drift factor for the ith determination.

15.4 Applying this equation to H and L produces the equations:

$$H = A_i H_i + a_i \quad (19)$$
$$L = A_i L_i + a_i \quad (20)$$

where:
H = the expected high value,
H_i = the measured high value,
L = the expected low value, and
L_i = the measured low value.

15.5 Each of A_i and a_i are expected to have a fixed and a variable component. Thus:

$$A_i = Ai + A' \quad (21)$$
$$a_i = ai + a' \quad (22)$$

15.6 Applying these to H and L produce the forms:

$$H = (Ai + A')H_i + ai + a' \quad (23)$$
$$L = (Ai + A')L_i + ai + a' \quad (24)$$

15.7 Separating out and combining terms gives a form that can be subject to a multi-variate least-squares fit. Thus:

$$H = AiH_i + A'H_i + ai + a' = A'H_i + ai + AiH_i + a' \quad (25)$$
$$L = AiL_i + A'L_i + ai + a' = A'L_i + ai + AiL_i + a' \quad (26)$$

15.8 The far right side of each equation (Eq 42, Eq 43) illustrates the order of columns to be fit in the spreadsheet as independent variables (H_i or L_i, i, iH_i or iL_i). The expected values form the column of the dependent variable (H, L). Thus, the monitor data for H and L are separated from the rest of the data to form four columns. The first column is the expected value column (H and L). The second column is the measured value column (H_i and L_i). The third column is the sequence number column (i), and the fourth column is the product of the values in columns two and three. A multi-variate least-squares fit of columns two, three, and four as independent variables against column one as dependent variable will produce the desired coefficients. The regression report will supply these parameters as follows: the constant = a', the first coefficient = A', the second coefficient = a, and the third coefficient = A.

15.9 The equation of application for drift correction becomes:

$$V_i^{'} = A'V_i + ai + AiV_i + a' \quad (27)$$

where:
$V_i^{'}$ = the drift corrected value for the ith determination, and
V_i = the uncorrected value for the ith determination.

15.10 By arranging the data in the original burn sequence and applying Eq 44, the data can be corrected for drift (see Notes 29 and 30).

15.11 Once the data has been drift corrected in this manner, it can be derandomized, entered in Table 2, and homogeneity determined as described in Section 12.

NOTE 31—If H and L are calibrants, then not only are all values drift corrected, but they are normalized, allowing an improved substitute for the procedure of Section 16.

16. Compositional Estimate by the Type Standard Method

16.1 It is often useful to not only determine whether or not a L/B is homogeneous, but to get a reasonable estimate of its composition for further use or processing. This is easily enough accomplished by utilizing the drift monitor data more fully. This is done by making sure the drift monitor is also a calibrant (reference material or certified reference material).

NOTE 32—The requirements for a drift monitor are primarily those of a standardant. It must be uniform and have a composition suitable for its application. It need not be a calibrant because it is only monitoring instrument drift behavior, which is only relative.

NOTE 33—There are cases where this method may be necessary. For example, there may be substantial time between run sequences that may produce different apparent compositions. Homogeneity tests should be run in as short a time span as possible to eliminate or reduce this potential effect.

NOTE 34—This method or that mentioned in Note 31 is best used for within-unit testing.

16.2 As in the scheme cited in Section 14, since only a single reference point is used, the analyst must decide whether to use an offset equation or a rotational equation.

16.3 The offset equation takes the form:

$$V_i^{``} = M - M_0 + V_i^{`} = M - M_0 + V_i - Ii \qquad (28)$$

where:

M = the concentration of the drift monitor and the other terms are as defined in Section 14.

16.4 The rotational equation becomes:

$$V_i^{``} = \frac{MV_i^{`}}{M_0} = \frac{MV_i}{M_0(1 + iI/M_0)} = \frac{MV_i}{M_0 + iI} \qquad (29)$$

where all the terms have their already defined meaning.

16.5 Once the data has been drift corrected and normalized in this manner, it can be derandomized, entered in Table 2, and homogeneity determined as described in Section 12.

17. Compositional Determination by the Multiple Calibrant Method

17.1 In Section 16, a means was outlined whereby a good compositional estimate might be produced. There are occasions when this is not sufficient. Not only is it necessary to determine whether a L/B is homogeneous, but it is also necessary to determine reasonably accurately what its composition is. In the following examples it is assumed that within-unit homogeneity has already been established. The proposed technique provides the additional information in the process of establishing between-unit homogeneity.

17.1.1 *Example #1*—A batch of samples is to be prepared for application to a proficiency testing program. The program administrator must be assured of between-unit homogeneity in order to assure every participant a "fair" sample. He must also have a knowledge of batch composition in order to assign the elements to be determined.

17.1.2 *Example #2*—In the preparation of a lot for development as a certified reference material, it is useful to know that it is homogeneous and whether or not the material has a composition suitable for the intended application. Such compositional information is useful in guiding the subsequent interlaboratory testing program that provides the data for the final compositional estimates. It also provides a basis for producing an estimate of the contribution to the compositional uncertainties caused by heterogeneity.

NOTE 35—This method is best used for between-unit testing.
NOTE 36—It is often suitable to normalize the data as in Section 16 (see Note 31) before applying this method.

17.2 Drift correction must be performed as described in Sections 13 through 15.

17.3 The addition of a number of calibrants and the use of a least-squares fit of their drift corrected values will yield equations for the calculation of elemental composition. The calibrants are added and a new array formed (C_1, C_2, ... , C_m, P_1, P_2, ... , P_n where C_i is the ith calibrant and P_j is the jth P/S). If the drift monitor is a calibrant, it can provide an m + 1'th calibrant for the fit.

17.4 All members of the array are to be run in random order in each of several determination sequences.

17.5 Each determination sequence is drift corrected as described in Sections 13 through 15.

17.6 Each determination sequence is derandomized so as to have the drift corrected values correspond to the original array.

17.7 The sub-array of calibrant means is subject to a least-squares fit of determined versus certified values.

NOTE 37—The least-squares fit is not limited to a first degree polynomial. Polynomials of greater than third degree should not be used.

17.8 The parameters obtained from the fit are used to calculate concentration values for the drift corrected, derandomized values for the unknowns. The calculation is applied to every value so as to produce a matrix of values to be used in the ANOVA.

17.9 Once the data has been drift corrected, normalized, derandomized, and compositionally defined, it can be entered in Table 2 and homogeneity determined as described in Section 12.

17.10 A properly formatted report allows the production of a good deal of information about the L/B being tested. For example, some possible determined quantities are:

17.10.1 A calculated value for each specimen for each element.

17.10.2 A mean and standard deviation for each specimen sub-array for each element. This allows the reporting of composition and precision data for subsequent testing or use, or both.

17.10.3 Maximum, minimum, and difference data for the specimen sub-array.

17.10.4 The critical (w) value for comparison.

17.10.5 The standard accuracy of the fit (Std Acc):

$$\left(\sqrt{\frac{\sum_{i=1}^{n} (C_i - \hat{C}_i)^2}{(n - 1 - d)}} \right) \qquad (30)$$

where:

n = the number of specimens in the sub-array,
C_i = the ith certified value,
$\hat{C}_i$ = the ith calculated value, and
d = the degree of the fit.

17.11 As can be seen, not only is homogeneity evaluated, but information about the accuracy and precision of the L/B composition is available.

17.12 The process described in this section is that of calibration. The analyst is able to do an "on-the-fly" calibration of the system under consideration. Added to the native calibration of the instrument, a reasonably accurate estimate of the L/B composition can be assigned along with an estimate of the quality of the estimate.

18. Determination of a Homogeneous Subset

18.1 Occasionally, the application of this procedure will result in the conclusion that a L/B is not homogeneous. It may still be possible to determine a viably homogeneous subset of the original population from which the test specimens were drawn.

18.2 If the test specimens were drawn using a systematic approach (for example, the ends of a set of bars whose processing history is known or can be assumed predictable), then it can be determined whether a subset of the original population can be found that is homogeneous.

18.3 If the test specimens were drawn using a fully random approach, but the original population is properly documented (for example, a number of cast pieces from a series of molds), then it can be determined whether a subset of the original population can be found that is homogeneous.

18.4 The basis for this approach is the determination of the specimen(s) causing the failure, eliminating it/them, reconfiguring the ANOVA for the reduced set, and retesting for homogeneity.

18.5 To apply this approach the grand mean of the specimen sub-array must be determined and a column added to the ANOVA that indicates the difference between each specimen mean and the grand mean. This could be considered a measure of each specimen's bias.

18.6 The specimen that causes the largest deviation (bias) is located and eliminated from the ANOVA. The ANOVA is reprocessed for the reduced subset and a determination of homogeneity (yes or no) made.

18.7 This elimination process is continued until a subset is arrived at that does satisfy the homogeneity criteria.

18.8 The original population is reexamined to see if a population subset can be selected that is homogeneous.

NOTE 38—A useful approach is to complete the process as given in this section, mark those specimens that do not conform, reconstitute the original matrix, and sort on the elements that caused the problem. Often the sorted data will suggest a "natural" subdivision of the original population.

NOTE 39—This procedure is not limited to L/B homogeneity studies. 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, 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.

NOTE 40—It is also possible to use this elimination process to discard a P/S which generates one or more outliers. The discarded P/S can be examined later for the cause of the outlier.

19. Precision and Bias

19.1 Precision data for this practice will be developed in the future if they are determined necessary.

20. Keywords

20.1 atomic emission spectroscopy; homogeneity; reference materials

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APPENDIXES

(Nonmandatory Information)

X1. EXAMPLE 1 TO ILLUSTRATE THIS PROCEDURE

X1.1 *Specimen Selection*—Suppose a material lot to be tested contains 50 specimens, each of them numbered consecutively. For ease of presentation in this example, only 6 specimens from the set of 50 will be considered instead of 15. The six are selected using a table of random numbers (see Table 1). From the table, select an arbitrary starting point and read in any direction using only numbers less than 50. For example, look across the top row of Table 1 to number 71, then down to number 22. From this starting point, reading down that column the numbers would be 22, 33, 47, 25, 12, and 10. The specimens having these numbers would be used for testing.

X1.2 *Test Procedure A (Drift Monitor)*—The six specimens are measured for element A in random order. The measurements are repeated six times, taking care to select the specimens in random order each time. A drift monitor (M) is measured with the specimens. Selecting a control frequency of three, for example, the complete measurement scheme can be represented as follows (reading down each column):

Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
M_1	M_4	M_7	M_{10}	M_{13}	M_{16}
22	25	10	12	47	33

Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
33	47	22	25	33	12
47	10	12	22	25	47
M_2	M_5	M_8	M_{11}	M_{14}	M_{17}
25	33	47	33	10	25
10	12	33	47	12	22
12	22	25	10	22	10
M_3	M_6	M_9	M_{12}	M_{15}	M_{18}

where M_1, M_2, M_3, ..., M_{18} determinations of the drift monitor run in chronological order.

X1.3 *Test for Instrumental Drift*—The data from the drift monitor are arranged in chronological order and D, and d, are calculated as tabulated in Table X1.1.

X1.3.1 Calculate:

$$S_1^2 = \sum D^2/(n-2) = 15.53/(18-1) = 0.914$$

X1.3.2 Calculate:

$$S_2^2 = \sum d^2/(n-1) = 17.920/(18-1) = 1.0541$$

X1.3.3 Calculate:

$$R = S_1^2/S_2^2 = 0.914/1.0541 = 0.867$$

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TABLE X1.1 Tabulation of Monitor, D, and _d_ Values

Monitor	D	D^2	d	d^2
$M_1 = 62.0$	-0.600	0.360	-1.0333	1.0678
$M_2 = 61.4$	0.600	0.360	-1.6333	2.6678
$M_3 = 62.0$	1.200	1.44	-1.0333	1.0678
$M_4 = 63.2$	-1.800	3.24	0.1666	0.0278
$M_5 = 61.4$	0.600	0.360	-1.6333	2.6678
$M_6 = 62.0$	1.200	1.44	-1.0333	1.0678
$M_7 = 63.2$	-0.600	0.360	0.1666	0.0278
$M_8 = 62.6$	1.300	1.69	-0.4333	0.1878
$M_9 = 63.9$	-1.300	1.69	0.8666	0.7511
$M_{10} = 62.6$	0.00	0.00	-0.4333	0.1878
$M_{11} = 62.6$	0.600	0.360	-0.4333	0.1878
$M_{12} = 63.2$	1.300	1.69	0.1666	0.0278
$M_{13} = 64.5$	-1.300	1.69	1.4666	2.1511
$M_{14} = 63.2$	0.700	0.490	0.1666	0.0278
$M_{15} = 63.9$	0.00	0.00	0.8666	0.7511
$M_{16} = 63.9$	0.600	0.360	0.8666	0.7511
$M_{17} = 64.5$	0.00	0.00	1.4666	2.1511
$M_{18} = 64.5$	...	...	1.4666	2.1511

Average = 63.0333; ΣD^2 = 15.53; Σd^2 = 17.920

TABLE X1.2 Drift-Corrected Measurements

Run	Specimen	Observed Measurement	Drift Factor	Corrected Measurements
1	22	48.8	0.9952	49.0
	33	48.7	0.9952	48.9
	47	50.9	0.9952	51.1
	25	49.7	0.9952	49.9
	10	48.8	0.9952	49.0
	12	48.7	0.9952	48.9
2	25	50.2	1.0048	49.9
	47	49.1	1.0048	48.9
	10	49.3	1.0048	49.0
	33	49.8	0.9952	50.0
	12	48.7	0.9952	48.9
	22	49.7	0.9952	49.9
3	10	49.7	1.0145	48.9
	22	50.8	1.0145	50.0
	12	50.9	1.0145	50.2
	47	51.0	1.0202	49.9
	33	51.2	1.0202	50.2
	25	52.1	1.0202	51.1
4	12	49.5	1.0097	49.0
	25	49.4	1.0097	48.9
	22	51.6	1.0097	51.1
	33	50.7	1.0145	49.9
	47	50.6	1.0145	49.9
	10	49.8	1.0145	49.0
5	47	52.6	1.0298	51.1
	33	52.5	1.0298	50.9
	25	52.4	1.0298	50.9
	10	51.3	1.0250	50.0
	12	51.2	1.0250	49.9
	22	53.1	1.0250	51.8
6	33	50.7	1.0355	48.9
	12	53.8	1.0355	51.9
	47	54.9	1.0355	53.0
	25	53.1	1.0403	51.0
	22	53.0	1.0403	50.9
	10	55.0	1.0403	52.9

X1.3.4 Since the ratio 0.867 is smaller than the ratio for $n = 18$ from Table 4 (interpolated value = 1.26), there is sufficient evidence at the 95 % confidence level to indicate that drift has indeed occurred.

X1.3.5 _Calculation of Drift Factors_—The sum of $M1 + M2$ is computed and divided by $2M1$, etc., as shown in the following:

$F_1 = (M_1 + M_2)/2M_1 = 0.9952$ $F_7 = (M_{10} + M_{11})/2M_1 = 1.0097$
$F_2 = (M_2 + M_3)/2M_1 = 0.9952$ $F_8 = (M_{11} + M_{12})/2M_1 = 1.0145$
$F_3 = (M_4 + M_5)/2M_1 = 1.0048$ $F_9 = (M_{13} + M_{14})/2M_1 = 1.0298$
$F_4 = (M_5 + M_6)/2M_1 = 0.9952$ $F_{10} = (M_{14} + M_{15})/2M_1 = 1.0250$
$F_5 = (M_7 + M_8)/2M_1 = 1.0145$ $F_{11} = (M_{16} + M_{17})/2M_1 = 1.0355$
$F_6 = (M_8 + M_9)/2M_1 = 1.0202$ $F_{12} = (M_{17} + M_{18})/2M_1 = 1.0403$

X1.3.6 The observed measurements are divided by the appropriate drift factors calculated in X1.3.5 to obtain corrected measurements as shown in Table X1.2.

X1.3.7 The corrected measurements are entered in Table X1.3.

NOTE X1.1—To facilitate the calculations in this example, the corrected values are rounded to the nearest whole number.

X1.4 _Test for Homogeneity Utilizing Procedure A_:

X1.4.1 Compute T_j, T_j^2, B_i, B_i^2, X_j^2, $t_j^{'}$, G, G^2 (see Table X1.3).

X1.4.2 Choose $\alpha = 0.05$ (95 % confidence level).

X1.4.3 Calculate $n = (b - 1)(t - 1) = (6 - 1)(6 - 1) = 25$.

X1.4.4 Determine the q value from Table 3 for $n = 25$ and $t = 6 ... q = 4.36$.

X1.4.5 Compute:

$$SSt = \left[\sum T_j^2/b\right] - (G^2/tb) = [(15012 + 14808 + 15307 + 15204 + 14903 + 15412)/6] - (3261636/36) = 4.333$$

X1.4.6 Compute:

$$SSb = \left[\sum B_i^2/t\right] - (G^2/tb) = [(88209 + 88209 + 90000 + 88804 + 93025 + 95481)/6] - (3261636/36) = 20.333$$

X1.4.7 Compute:

$$SST = \sum X_j^2 - (G^2/tb) = (15012 + 14808 + 15307 + 15204 + 14903 + 154120) - (3261636/36) = 45.000$$

X1.4.8 Compute:

$$s = \sqrt{\frac{(SST - SSb - SSt)}{(b - 1)(t - 1)}} = \sqrt{\frac{(45.000 - 20.333 - 4.333)}{(5)(5)}} = 0.90186$$

X1.4.9 Compute:

$$w = qs/\sqrt{b} = (4.36)(0.90186)/\sqrt{6} = (4.36)(0.90186)/2.449 = 1.605$$

TABLE X1.3 Example for Homogeneity Testing (Procedure A)

Specimen	1	2	3	4	5	6	T	T^2	X^2	t'
10	49	49	50	49	50	53	299	89401	15012	49.8
12	49	49	49	49	50	52	299	89401	14808	49.8
22	49	50	50	51	52	51	303	91809	15307	50.5
25	50	50	51	49	51	51	302	91204	15204	50.3
33	49	50	50	50	51	49	299	89401	14903	49.8
47	51	49	50	50	51	53	304	92416	15412	50.7
B	297	297	300	298	305	309				
B^2	88209	88209	90000	88804	93025	95481	G = 1806.0		G^2 = 3261636	

X1.4.10 The maximum difference between any of the mean $t_j^{'}$ values in Table X1.3 (Procedure A) equals 0.87. Since 0.87 does *not* exceed the *w* computed value of 1.605, there is evidence at the 95 % confidence level that the specimens are homogeneous.

X1.4.11 An evaluation of the overall quality of the data in Table X1.3 (Procedure A) can be made by computing the relative standard deviation (*RSD*) as follows: $RSD = s/t' \times 100$ where *s* is computed in X1.4.8 and *t'* is the grand mean for the entire system. For the above example, $RSD = 0.90186/50.16 \times 100 = 1.80 \%$.

X1.5 *Test Procedure B (No Drift Monitor)*—The six specimens are measured for element B in random order. The measurements are repeated six times, taking care to select the specimens in random order each time. For example, the complete measurement scheme can be represented as follows (reading down each column):

Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
22	25	10	12	47	33
33	47	22	25	33	12
47	10	12	22	25	47
25	33	47	33	10	25
10	12	33	47	12	22
12	22	25	10	22	10

X1.5.1 The measurements for each element are entered in Table X1.4.

X1.6 *Test for Homogeneity Utilizing Procedure B*:

X1.6.1 Compute T_j, T_j^2, B_i, B_i^2, X_j^2, $t_j^{'}$, G, G^2 (see Table X1.4).

X1.6.2 Choose $\alpha = 0.05$ (95 % confidence level).

X1.6.3 Calculate $n = (b - 1)(t - 1) = (6 - 1)(6 - 1) = 25$.

X1.6.4 Determine the *q* value from Table 3 for $n = 25$ and $t = 6 ... q = 4.36$.

X1.6.5 Compute:

$$SSt = \left[\sum T_j^2/b\right] - (G^2/tb) = [(75.673 + 75.533 + 74.218 + 77.405$$
$$+ 75.429 + 76.021)/6] - (2725.571/36) = 0.00291$$

X1.6.6 Compute:

$$SSb = \left[\sum B_i^2/t\right] - (G^2/tb) = [(77.792 + 76.073 + 75.794 + 75.221$$
$$+ 77.106 + 72.335)/6] - (2725.571/36) = 0.01004$$

X1.6.7 Compute:

$$SST = \sum X_j^2 - (G^2/tb) = (12.617 + 12.595 + 12.373 + 12.905 + 12.578$$
$$+ 12.678) - (3261636/36) = 0.03589$$

X1.6.8 Compute:

$$s = \sqrt{\frac{(SST - SSb - SSt)}{(b - 1)(t - 1)}} = \sqrt{\frac{(0.03589 - 0.01004 - 0.00291)}{(5)(5)}}$$
$$= 0.03029$$

X1.6.9 Compute:

$$w = qs/\sqrt{b} = (4.36)(0.03029)/\sqrt{6} = (4.36)(0.03029)/2.449 = 0.0539$$

X1.6.10 The maximum difference between any of the mean $t_j^{'}$ values in Table X1.4 (Procedure B) equals 0.0305. Since 0.0305 does *not* exceed the *w* computed value of 0.0539, there is evidence at the 95 % confidence level that the specimens are homogeneous.

X1.6.11 An evaluation of the overall quality of the data in Table X1.4 (Procedure B) can be made by computing the relative standard deviation (*RSD*) as follows: $RSD = s/t' \times 100$ where *s* is computed in X1.6.8 and *t'* is the grand mean for the entire system. For the above example, $RSD = 0.03029/1.450 \times 100 = 2.09 \%$.

X2. EXAMPLE 2 TO ILLUSTRATE THIS PROCEDURE

X2.1 *Explanation of Need for Application of This Practice*—For a particular quarter of the ASTM Proficiency Testing Program (PTP), 82 participants were registered. Two batches of specimens were prepared for the participants. Five additional specimens were prepared for each batch to allow for additions or errors for a total of 87 specimens each. The specimens were taken from a parent lot that had already been tested for within and between-unit homogeneity. Thus, it was only necessary to provide assurance that the batches were sufficiently uniform for the intended application. This would assure every participant of a "fair" pair of specimens. It would also assure the administrator that the principle source of non-random variation was from participant activities. That is, it would assure that the principle variation determinant was from the participants and that each would have a valid measure of his performance.

NOTE X2.1—This application demonstrates the utility of the method. Here, there is no intent that a reference material be produced. The homogeneity information assures sample fairness, while the composition information provides the administrator with element selection criteria.

TABLE X1.4 Example for Homogeneity Testing (Procedure B)

Specimen	1	2	3	4	5	6	T	T^2	X^2	t'
10	1.447	1.486	1.470	1.440	1.457	1.399	8.699	75.673	12.617	1.450
12	1.458	1.503	1.403	1.437	1.459	1.431	8.691	75.533	12.595	1.449
22	1.470	1.417	1.426	1.428	1.469	1.405	8.615	74.218	12.373	1.436
25	1.482	1.480	1.508	1.438	1.459	1.431	8.798	77.405	12.905	1.466
33	1.461	1.445	1.468	1.485	1.446	1.380	8.685	75.429	12.578	1.448
47	1.502	1.391	1.431	1.445	1.491	1.459	8.719	76.021	12.678	1.453
B	8.820	8.722	8.706	8.673	8.781	8.505				
B^2	77.792	76.073	75.794	75.221	77.106	72.335	G = 52.207		G^2 = 2725.571	

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NOTE X2.2—The tables presented in examples Appendix X2, Appendix X3, and Appendix X4 are for guideline purposes only. They are examples of working documents (internal reports) and there is no intent that a final statement of content or uncertainty is stated or implied. An analyst wanting to take a report to a higher level is expected to follow the requirements of ISO Guides 35 and 98 (GUM).

X2.2 *Specimen Preparation*—Two round bars from two different heats had previously been purchased and examined for homogeneity and composition for this application. The material selected was F-11 and was being applied to the Plain Carbon & Alloy Steel program for that quarter. Eighty-seven 10-mm specimens were cut from each bar on an automated band saw. Specimens were captured in a box, their sides sand blasted, their faces planed with a swing grinder, and their sides marked with the batch identification using a permanent marker. Each batch was processed separately.

X2.3 *Batch Homogeneity Specimen Selection*—No effort was made to maintain the order of production of the batch specimens, so any selection process would draw from an already randomized population.

X2.3.1 Specimens were randomly drawn from the box and labeled 1–87 with a permanent marker on one face.

X2.3.2 A spreadsheet template was activated for each batch, dedicated to its case, and saved with the name of its PTP designation.

X2.3.3 The spreadsheet random function was used to select 15 specimens for the batch homogeneity check.

X2.3.4 The specimens selected were numbers: 3, 8, 14, 16, 22, 24, 31, 51, 52, 62, 66, 71, 72, 73, 85.

X2.4 *Specimen Verification*—All specimens were compared to the lot master using an atomic emission spectrometer (Spark-AES).

X2.4.1 A hardcopy record of the comparison was produced and archived for reference in case of questions as to the authenticity of all specimens used in the program quarter.

X2.4.2 Specimens to be used for the batch homogeneity check were segregated for further testing.

X2.4.3 The remaining specimens were returned to the box.

X2.5 *Calibrant Selection*—Nine calibrants were selected for the composition phase of the homogeneity study, which was performed according to the procedure described in Section 17.

X2.5.1 These calibrants were: NIST 1228, NIST 1263A, SS 432/1, ECRM 195-1D, BS 12B, BS 45A, BS 55E, BS 230, BS 1981.

X2.5.2 BS 1981 was selected to be the drift monitor.

X2.6 *Data Generation*—A Spark-AES unit, which has been configured to produce reasonably stable output over long analytical runs, was prepared for the studies.

X2.6.1 Determination sequence charts, produced by the dedicated spreadsheets, were utilized to guide the determination sequences for the studies (see Table X2.1).

X2.6.2 Each determination was executed according to the determination sequence charts and the determinations captured in a database on the Spark-AES's hard drive.

TABLE X2.1 Determination Sequence Chart

			Monitor = BS 1981			
Sample	Position	Burn	Run 1	Run 2	Run 3	Run 4
Monitor	M	1	M	M	M	M
NIST 1228	1	2	14	11	14	9
NIST 1263A	2	3	21	22	20	15
SS 432/1	3	4	1	9	10	19
E195-1D	4	5	12	17	21	14
Monitor	M	6	M	M	M	M
BS 12B	5	7	20	4	16	12
BS 45A	6	8	10	18	18	23
BS 55E	7	9	22	12	11	7
BS 230	8	10	11	7	7	2
Monitor	M	11	M	M	M	M
#3	9	12	3	10	4	18
#8	10	13	15	3	19	11
#14	11	14	18	20	15	20
#16	12	15	19	5	1	17
Monitor	M	16	M	M	M	M
#22	13	17	6	6	3	3
#24	14	18	23	13	6	21
#31	15	19	13	23	8	10
#51	16	20	7	16	22	4
Monitor	M	21	M	M	M	M
#52	17	22	5	2	5	5
#62	18	23	8	15	2	6
#66	19	24	4	19	23	13
#71	20	25	9	21	12	22
Monitor	M	26	M	M	M	M
#72	21	27	16	8	13	1
#73	22	28	2	1	9	16
#85	23	29	17	14	17	8
Monitor	M	30	M	M	M	M

TABLE X2.2 Final Batch Report—For Some Elements

Sample	C	Mn	P	S	Si	Cu	Ni	Cr	V	Mo
#3	0.124	0.437	0.0032	0.0120	0.562	0.183	0.121	1.15	0.0030	0.519
#8	0.125	0.435	0.0035	0.0130	0.555	0.183	0.119	1.15	0.0029	0.520
#14	0.126	0.437	0.0032	0.0134	0.558	0.183	0.120	1.15	0.0030	0.524
#16	0.125	0.436	0.0035	0.0126	0.557	0.182	0.119	1.15	0.0030	0.520
#22	0.126	0.439	0.0033	0.0134	0.560	0.184	0.121	1.15	0.0030	0.522
#24	0.125	0.437	0.0036	0.0129	0.562	0.184	0.121	1.15	0.0031	0.522
#31	0.129	0.437	0.0033	0.0130	0.563	0.185	0.122	1.14	0.0030	0.519
#51	0.126	0.436	0.0032	0.0128	0.567	0.185	0.122	1.15	0.0030	0.521
#52	0.125	0.437	0.0034	0.0123	0.556	0.183	0.120	1.15	0.0031	0.521
#62	0.124	0.435	0.0033	0.0132	0.560	0.183	0.121	1.15	0.0030	0.521
#66	0.126	0.438	0.0035	0.0136	0.563	0.184	0.121	1.15	0.0030	0.522
#71	0.124	0.436	0.0035	0.0129	0.558	0.183	0.120	1.15	0.0030	0.519
#72	0.126	0.437	0.0039	0.0133	0.562	0.184	0.121	1.15	0.0031	0.523
#73	0.125	0.436	0.0033	0.0131	0.561	0.184	0.121	1.15	0.0030	0.522
#85	0.125	0.436	0.0034	0.0129	0.562	0.184	0.120	1.14	0.0029	0.519
Avg Unk	0.125	0.436	0.0034	0.0129	0.560	0.183	0.120	1.15	0.0030	0.521
Std Dev	0.001	0.001	0.0002	0.0004	0.003	0.001	0.001	<0.01	0.0001	0.002
RSD	0.80	0.23	5.88	3.1	0.54	0.55	0.83	–	3.33	0.38
Std Acc	0.010	0.008	0.0008	0.0011	0.008	0.003	0.004	0.01	0.0019	0.005
Maximum	0.129	0.439	0.0039	0.0136	0.567	0.185	0.122	1.15	0.0031	0.524
Minimum	0.124	0.435	0.0032	0.0120	0.555	0.182	0.119	1.14	0.0029	0.519
T	0.005	0.004	0.0007	0.0016	0.012	0.003	0.003	0.01	0.0002	0.005
W	0.006	0.008	0.0010	0.0018	0.016	0.005	0.005	0.01	0.0004	0.008

X2.6.3 The drift monitor was run seven times in each determination sequence.

X2.6.4 Each calibrant/specimen array of 23 units was subdivided into five groups of four and one group of three.

X2.6.5 The drift monitor was run at the beginning of each sequence and after each grouping.

X2.7 *Data Processing*—Data from the studies were extracted from the Spark-AES database and converted to a spreadsheet readable form.

X2.7.1 Each study data batch was read into its spreadsheet and processed accordingly.

X2.7.2 Each spreadsheet template contains all generic information necessary for processing the data from a homogeneity study. The template is customized for the case under consideration and saved in its customized form. All actions associated with this practice are fully automated through the use of spreadsheet macros.

X2.7.3 The data from each batch was processed on an element by element basis.

X2.7.4 For each element the data from the four sequences was drift corrected, derandomized, and normalized in accordance with Sections 14 and 16.

X2.7.5 The analyst checked the data for proper placement (properly derandomized).

X2.7.6 For each element, the analyst executed a least-squares fit and examined the results on a correlation chart. If indicated, a higher degree fit was selected.

X2.7.7 For each element, the fit coefficients were applied to the specimens and a statistical report for that element presented to the analyst for examination.

X2.7.8 When all elements had been so processed, a final report was produced and printed (see Table X2.2). Three copies were produced: one for the analyst's records, one for the company records, and one for the ASTM PTP administrator.

NOTE X2.3—In each of the final reports, T = the maximum difference between means (max—min) and W = the critical value (*w*).

X2.8 *Final Preparation and Shipping*—The study specimens were returned to the box with the other specimens.

X2.8.1 Each specimen was labeled on the non-analytical face with its PTP identification number using a scribing machine.

X2.8.2 Specimens from both batches were paired and packaged for shipping.

X2.8.3 Packages were shipped to participants for participation in the quarter's program.

X3. EXAMPLE 3 TO ILLUSTRATE THIS PROCEDURE

X3.1 *Explanation of Need for Application of This Practice*—A reference material producer obtained a lot of 16 short bars to be developed as a commercially pure iron standardant. In order to assure users of uniformity of results and product, within-unit and between-unit homogeneity studies were performed. Compositional information was produced so as to provide users with pertinent information.

NOTE X3.1—This application further demonstrates the utility of the method. Again, there is no intent that a reference material be produced. The homogeneity information assures the user it will continue to be useful as a standardant throughout its life span. Moreover, replacements from the same batch will perform similarly. Composition information provides the user with element/line selection criteria (high, low, line).

X3.2 *Specimen Preparation*—The sixteen bars were approximately 2 in. (51 mm) square and 17 in. (432 mm) long. They had been produced using a continuous casting method, rolled, and cut to the present configuration. Because of the known lot history and the individual bar size, it was deemed sufficient to only sample one end of each bar.

X3.2.1 The bars were labeled A–P and a sample taken from one end of each bar.

X3.2.2 Samples were captured in a box, their faces planed with a swing grinder, and their sides marked with the lot identification using an etching tool.

X3.3 *Within-Unit Homogeneity Testing*—Samples A, H, and P were selected for within-unit homogeneity testing.

X3.3.1 A spreadsheet template was activated for the three, dedicated to this case, and saved with the name of this application.

X3.3.2 The dedicated spreadsheet was configured to accommodate a two inch square sample. Nine locations were to be tested on one face of each sample (see Fig. X3.1). Spots 1, 3, 5, and 7 were to be at the four corners of the face. Spots 2, 4, 6, and 8 were to be midway between the corner spots adjacent to the "flat" sides of the face. Spot 9 was to be in the middle of the face. The eight peripheral spots were sufficiently interior to the edges of each sample so as to assure a good seal on the plate of Spark-AES unit.

X3.3.3 The calibrant BS 50A was selected as the drift monitor.

X3.3.4 A Spark-AES unit, which has been configured to produce reasonably stable output over long analytical runs, was prepared for the study.

X3.3.5 The drift monitor was burned at the beginning of each sequence and after every group of three for a total of four determinations per sequence. Four runs were made for each sample for a total of twelve runs. Sequences were those given in the sequence chart generated by the dedicated spreadsheet (see Table X3.1).

X3.3.6 Determinations were captured in a database on the Spark-AES's hard drive.
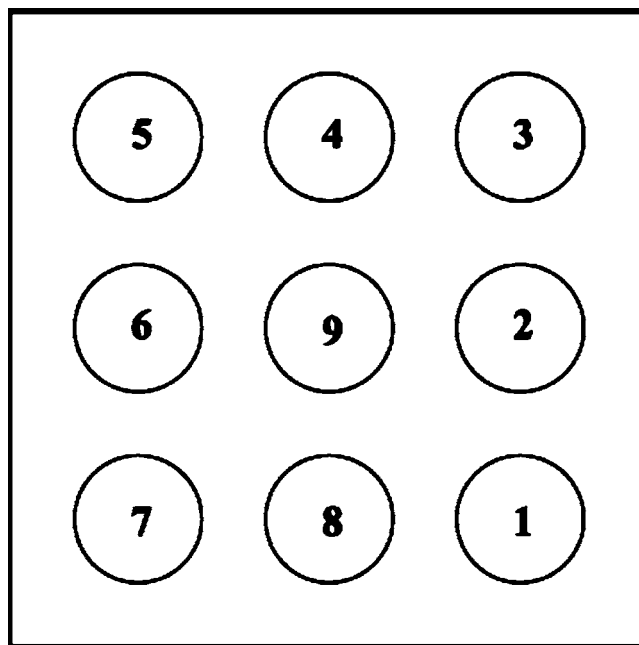
FIG. X3.1 Spot Placement on a Square Sample for Within-Unit Homogeneity Testing

X3.3.7 Upon completion of all determinations, the study data were extracted from the Spark-AES database and converted to a spreadsheet readable form.

X3.3.8 The study data were read into the dedicated spreadsheet and processed accordingly.

X3.3.9 Each spreadsheet template contains all generic information necessary for processing the data from a homogeneity study. The template is customized for the case under consideration and saved in its customized form. All actions associated with this practice are fully automated through the use of spreadsheet macros.

X3.3.10 For each sample the data were checked for proper burn position placement.

X3.3.11 For each element a significance test was performed. If the concentration or the overall relative standard deviation were too small, the element was discarded from the study.

X3.3.12 The data from the surviving elements were processed on an element by element basis.

X3.3.13 For the first element of the first sample (A) the data from the four sequences were drift corrected, derandomized, and normalized in accordance with Sections 14 and 16, and presented to the analyst for examination.

X3.3.14 The analyst checked the presented data for proper placement (properly derandomized).

X3.3.15 The analyst authorized the spreadsheet to process the remaining elements of the first sample.

X3.3.16 The analyst processed the remaining two samples in the same manner.

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TABLE X3.1 Determination Sequence Chart for Within-Unit Homogeneity Testing (Square)

Monitor = BS 50A					
A					
Loc	Brn	R-l	R-2	R-3	R-4
Mon	1	M	M	M	M
#1	2	6	2	5	4
#2	3	9	8	8	9
#3	4	3	3	4	7
Mon	5	M	M	M	M
#4	6	7	7	9	3
#5	7	1	6	3	2
#6	8	2	5	1	5
Mon	9	M	M	M	M
#7	10	4	4	6	1
#8	11	8	9	7	6
#9	12	5	1	2	8
Mon	13	M	M	M	M
H					
Loc	Brn	R-l	R-2	R-3	R-4
Mon	1	M	M	M	M
#1	2	6	2	5	4
#2	3	9	8	8	9
#3	4	3	3	4	7
Mon	5	M	M	M	M
#4	6	7	7	9	3
#5	7	1	6	3	2
#6	8	2	5	1	5
Mon	9	M	M	M	M
#7	10	4	4	6	1
#8	11	8	9	7	6
#9	12	5	1	2	8
Mon	13	M	M	M	M
P					
Loc	Brn	R-l	R-2	R-3	R-4
Mon	1	M	M	M	M
#1	2	6	2	5	4
#2	3	9	8	8	9
#3	4	3	3	4	7
Mon	5	M	M	M	M
#4	6	7	7	9	3
#5	7	1	6	3	2
#6	8	2	5	1	5
Mon	9	M	M	M	M
#7	10	4	4	6	1
#8	11	8	9	7	6
#9	12	5	1	2	8
Mon	13	M	M	M	M

Where Loc = Location, Mon = Monitor, Brn = Burn number, R-1 = Run #1, R-2 = Run #2, etc.

X3.3.17 When all samples had been so processed, a final report was produced and printed. Two copies were produced: one for the analyst's records and one for the company records.

X3.4 *Between-Unit Homogeneity Testing*—Samples A, H, and P were restored to the original collection of 16 and the entire group prepared for lot homogeneity testing.

X3.4.1 A spreadsheet template was activated for the group, dedicated to this case, and saved with the name of this application.

X3.4.2 *Calibrant Selection*—Nine calibrants were selected for the composition phase of the homogeneity study, which was performed according to the procedure described in Section 17. These calibrants were: NIST 1765, NIST 1766, NIST 1767, SS 111, ECRM 097-1D, SUS FE1/1, VASKUT B20, BS 50D, and BS 50A. BS 50A was selected as the drift monitor.

X3.4.3 *Data Generation*—A Spark-AES unit, which has been configured to produce reasonably stable output over long analytical runs, was prepared for the studies.

X3.4.4 Determination sequence charts, produced by the dedicated spreadsheets, were utilized to guide the determination sequences for the studies (see Table X3.2).

X3.4.5 Each determination was executed according to the determination sequence charts and the determinations captured in a database on the Spark-AES's hard drive.

X3.4.6 The drift monitor was run seven times in each determination sequence.

X3.4.7 Each calibrant/specimen array of 24 units was subdivided into six groups of four.

X3.4.8 The drift monitor was run at the beginning of each sequence, and after each group of four.

X3.5 *Data Processing*—Data from the study were extracted from the Spark-AES database and converted to a spreadsheet readable form.

X3.5.1 The study data were read into the spreadsheet and processed accordingly.

X3.5.2 The spreadsheet template contains all generic information necessary for processing the data from a homogeneity study. The template is customized for the case under consideration and saved in its customized form. All actions associated with this practice are fully automated through the use of spreadsheet macros.

X3.5.3 The data from the study was processed on an element by element basis.

X3.5.4 For each element the data from the four sequences was drift corrected, derandomized, and normalized in accordance with Sections 14 and 16, and presented to the analyst for examination.

X3.5.5 The analyst checked the presented data for proper placement (properly derandomized).

X3.5.6 The analyst executed a least-squares fit and examined the results on a correlation chart. If indicated, a higher degree fit was selected.

X3.5.7 The fit coefficients were applied to the specimens and a statistical report presented to the analyst for examination.

X3.5.8 When all elements had been so processed, a final report was produced and printed (see Table X3.3). Two copies were produced: one for the analyst's records and one for the company records.

X3.6 *Generation of Two Homogeneous Subsets*—Examination of the report indicated non-homogeneities had been discovered. Bold values were those that had been discarded, then added back as per the practice of Section 18.

X3.6.1 A sort of carbon (C), nickel (Ni), or chromium (Cr) revealed that the original 16 could be subdivided into two groups of similar composition with one bar transitional between the two. Cr produced the best sort (see Table X3.4).

TABLE X3.2 Determination Sequence Chart for Between-Unit Homogeneity Testing

Sample	Position	Burn	Run 1	Run 2	Run 3	Run 4
			Monitor = BS 50A			
Monitor	M	1	M	M	M	M
NIST 1765	1	2	14	15	20	2
NIST 1766	2	3	24	20	5	5
NIST 1767	3	4	9	21	6	7
SS 111	4	5	20	7	11	8
Monitor	M	6	M	M	M	M
ECRM 097-1D	5	7	3	23	23	20
SUS FE1/1	6	8	5	17	17	9
VASCUT B20	7	9	1	10	4	1
BS 50D	8	10	15	6	13	23
Monitor	M	11	M	M	M	M
A	9	12	7	8	16	13
B	10	13	6	4	24	16
C	11	14	21	12	14	6
D	12	15	10	16	2	10
Monitor	M	16	M	M	M	M
E	13	17	18	3	1	14
F	14	18	19	13	15	18
G	15	19	16	11	21	21
H	16	20	13	24	9	17
Monitor	M	21	M	M	M	M
I	17	22	22	9	19	15
J	18	23	2	19	12	24
K	19	24	12	2	18	11
L	20	25	23	18	8	3
Monitor	M	26	M	M	M	M
M	21	27	8	5	7	19
N	22	28	17	14	3	12
O	23	29	11	1	22	22
P	24	30	4	22	10	4
Monitor	M	31	M	M	M	M

TABLE X3.3 Pre-Split Lot Report—For Some Elements[A]

Sample	C	Mn	P	S	Si	Cu	Ni	Cr	V	Mo
A	0.0093	0.0594	0.0053	0.0037	0.0150	0.0098	0.0203	**0.0205**	0.0003	0.0014
B	0.0095	0.0591	0.0047	0.0034	0.0147	0.0094	0.0200	**0.0206**	0.0002	0.0016
C	0.0096	0.0595	0.0052	0.0037	0.0162	0.0101	0.0205	**0.0215**	0.0003	0.0017
D	0.0089	0.0582	0.0054	0.0039	0.0159	0.0094	0.0201	**0.0227**	0.0002	0.0014
E	0.0098	0.0593	0.0056	0.0040	0.0152	0.0097	0.0202	**0.0205**	0.0003	0.0016
F	0.0092	0.0595	0.0052	0.0036	0.0151	0.0099	0.0203	0.0204	0.0002	0.0014
G	0.0096	0.0594	0.0050	0.0036	0.0153	0.0101	0.0204	0.0204	0.0002	0.0014
H	**0.0079**	0.0596	0.0057	0.0035	0.0162	0.0096	**0.0222**	**0.0238**	0.0003	0.0018
I	**0.0077**	0.0593	0.0055	0.0033	0.0155	0.0092	**0.0218**	**0.0235**	0.0003	0.0016
J	**0.0077**	0.0595	0.0056	0.0034	0.0157	0.0092	**0.0221**	**0.0235**	0.0003	0.0016
K	0.0099	0.0597	0.0050	0.0036	0.0161	0.0099	0.0205	**0.0213**	0.0003	0.0015
L	**0.0077**	0.0593	0.0054	0.0033	0.0156	0.0093	**0.0219**	**0.0236**	0.0003	0.0017
M	**0.0078**	0.0593	0.0052	0.0034	0.0155	0.0091	**0.0217**	**0.0236**	0.0003	0.0017
N	0.0095	0.0593	0.0053	0.0038	0.015	0.0098	0.0202	**0.0208**	0.0003	0.0017
O	**0.0079**	0.0593	0.0054	0.0034	0.0157	0.0092	**0.0222**	**0.0239**	0.0004	0.0016
P	0.0096	0.0592	0.0054	0.0037	0.0148	0.0095	0.0202	0.0204	0.0002	0.0014
Avg Unk	0.0095	0.0593	0.0053	0.0036	0.0155	0.0096	0.0203	0.0204	0.0003	0.0016
Std Dev	0.0003	0.0004	0.0003	0.0002	0.0005	0.0003	0.0002	<0.0001	0.0001	0.0001
RSD	3.16	0.67	5.66	5.56	3.23	3.13	0.99	–	33.33	6.25
Std Avg	0.0162	0.0655	0.0045	0.0046	0.0264	0.0173	0.0176	0.0229	0.0072	0.0074
Std Acc	0.0012	0.0014	0.0008	0.0002	0.002	0.0005	0.0005	0.0016	0.0002	0.0003
RSA	7.21	2.14	18.26	4.54	7.52	2.92	2.66	7.01	3.06	4.04
Maximum	0.0099	0.0597	0.0057	0.0040	0.0162	0.0101	0.0208	0.0204	0.0004	0.0018
Minimum	0.0089	0.0582	0.0047	0.0033	0.0147	0.0091	0.02	0.0204	0.0002	0.0014
T	0.0010	0.0015	0.0010	0.0007	0.0015	0.0010	0.0008	0	0.0002	0.0004
W	0.0013	0.0017	0.0016	0.0008	0.0016	0.0014	0.0011	0	0.0003	0.0005

[A] The **bold** cells are those that were eliminated to produce homogeneous subsets.

X3.6.2 Group one consisted of the nine bars A, B, C, E, F, G, K, N, and P.

X3.6.3 Group two consisted of the six bars H, I, J, L, M, and O.

TABLE X3.4 Sorted Lot—For Some Elements[A]

Sample	C	Mn	P	S	Si	Cu	Ni	Cr	V	Mo
A	0.0093	0.0594	0.0053	0.0037	0.0150	0.0098	0.0203	0.0205	0.0003	0.0014
B	0.0095	0.0591	0.0047	0.0034	0.0147	0.0094	0.0200	0.0206	0.0002	0.0016
C	0.0096	0.0595	0.0052	0.0037	0.0162	0.0101	0.0205	0.0215	0.0003	0.0017
E	0.0098	0.0593	0.0056	0.0040	0.0152	0.0097	0.0202	0.0205	0.0003	0.0016
F	0.0092	0.0595	0.0052	0.0036	0.0151	0.0099	0.0203	0.0204	0.0002	0.0014
G	0.0096	0.0594	0.0050	0.0036	0.0153	0.0101	0.0204	0.0204	0.0002	0.0014
K	0.0099	0.0597	0.0050	0.0036	0.0161	0.0099	0.0205	0.0213	0.0003	0.0015
N	0.0095	0.0593	0.0053	0.0038	0.0150	0.0098	0.0202	0.0208	0.0003	0.0017
P	0.0096	0.0592	0.0054	0.0037	0.0148	0.0095	0.0202	0.0204	0.0002	0.0014
D	**0.0089**	**0.0582**	**0.0054**	**0.0039**	**0.0159**	**0.0094**	**0.0201**	**0.0227**	**0.0002**	**0.0014**
H	**0.0079**	**0.0596**	**0.0057**	**0.0035**	**0.0162**	**0.0096**	**0.0222**	**0.0238**	**0.0003**	**0.0018**
I	**0.0077**	**0.0593**	**0.0055**	**0.0033**	**0.0155**	**0.0092**	**0.0218**	**0.0235**	**0.0003**	**0.0016**
J	**0.0077**	**0.0595**	**0.0056**	**0.0034**	**0.0157**	**0.0092**	**0.0221**	**0.0235**	**0.0003**	**0.0016**
L	**0.0077**	**0.0593**	**0.0054**	**0.0033**	**0.0156**	**0.0093**	**0.0219**	**0.0236**	**0.0003**	**0.0017**
M	**0.0078**	**0.0593**	**0.0052**	**0.0034**	**0.0155**	**0.0091**	**0.0217**	**0.0236**	**0.0003**	**0.0017**
O	**0.0079**	**0.0593**	**0.0054**	**0.0034**	**0.0157**	**0.0092**	**0.0222**	**0.0239**	**0.0004**	**0.0016**

[A] The **bold** cells are those that were eliminated to produce homogeneous subsets.

TABLE X3.5 First Group Report—For Some Elements

Sample	C	Mn	P	S	Si	Cu	Ni	Cr	V	Mo
A	0.0093	0.0598	0.0053	0.0037	0.0150	0.0098	0.0203	0.0197	0.0003	0.0014
B	0.0095	0.0595	0.0047	0.0034	0.0147	0.0094	0.0200	0.0198	0.0002	0.0016
C	0.0096	0.0599	0.0052	0.0037	0.0162	0.0101	0.0205	0.0207	0.0003	0.0017
E	0.0098	0.0596	0.0056	0.0040	0.0152	0.0097	0.0202	0.0197	0.0003	0.0016
F	0.0092	0.0599	0.0052	0.0036	0.0151	0.0099	0.0203	0.0196	0.0002	0.0014
G	0.0096	0.0599	0.0050	0.0036	0.0153	0.0101	0.0204	0.0196	0.0002	0.0014
K	0.0099	0.0601	0.0050	0.0036	0.0161	0.0099	0.0205	0.0205	0.0003	0.0015
N	0.0095	0.0597	0.0053	0.0038	0.0150	0.0098	0.0202	0.0200	0.0003	0.0017
P	0.0096	0.0597	0.0054	0.0037	0.0148	0.0095	0.0202	0.0197	0.0002	0.0014
Avg Unk	0.0095	0.0598	0.0051	0.0037	0.0153	0.0098	0.0203	0.0199	0.0002	0.0015
Std Dev	0.0002	0.0002	0.0003	0.0002	0.0005	0.0002	0.0002	0.0004	0.0001	0.0001
RSD	2.11	0.33	5.88	5.41	3.27	2.04	0.99	2.04	50.00	6.67
Std Avg	0.0162	0.0375	0.0045	0.0046	0.0264	0.0173	0.0176	0.0221	0.0072	0.0074
Std Acc	0.0012	0.0006	0.0008	0.0002	0.0020	0.0005	0.0005	0.0011	0.0002	0.0003
RSA	7.21	1.54	18.26	4.83	7.52	2.92	2.66	5.09	3.06	4.34
Maximum	0.0099	0.0601	0.0056	0.0040	0.0162	0.0101	0.0205	0.0207	0.0003	0.0017
Minimum	0.0092	0.0595	0.0047	0.0034	0.0147	0.0094	0.0200	0.0196	0.0002	0.0014
T	0.0007	0.0006	0.0009	0.0006	0.0015	0.0007	0.0005	0.0011	0.0001	0.0003
W	0.0013	0.0012	0.0017	0.0007	0.0017	0.0012	0.0011	0.0012	0.0003	0.0007

X3.6.4 Bar D was discarded.

X3.7 *Data Reprocessing*—Two new spreadsheets were created for the two groups from the lot homogeneity spreadsheet template.

X3.7.1 The study data were read into each spreadsheet and each was processed as before.

X3.7.2 Reports from the two were issued that confirmed the homogeneity of the two groups (see Tables X3.5 and X3.6). Two copies of each were produced as before.

X3.8 *Conversion to Stock*—The composition information from the group homogeneity studies was used to supply composition information for the Data Sheets issued.

X3.8.1 Data Sheets were issued for the two groups.

X3.8.2 Material was made available for interested users.

TABLE X3.6 Second Group Report—For Some Elements

Sample	C	Mn	P	S	Si	Cu	Ni	Cr	V	Mo
H	0.0079	0.0600	0.0057	0.0035	0.0162	0.0096	0.0222	0.0238	0.0003	0.0018
I	0.0077	0.0597	0.0055	0.0033	0.0155	0.0092	0.0218	0.0235	0.0003	0.0016
J	0.0077	0.0599	0.0056	0.0034	0.0157	0.0092	0.0221	0.0235	0.0003	0.0016
L	0.0077	0.0597	0.0054	0.0033	0.0156	0.0093	0.0219	0.0236	0.0003	0.0017
M	0.0078	0.0597	0.0052	0.0034	0.0155	0.0091	0.0217	0.0236	0.0003	0.0017
O	0.0079	0.0596	0.0054	0.0034	0.0157	0.0092	0.0222	0.0239	0.0004	0.0016
Avg Unk	0.0078	0.0598	0.0055	0.0034	0.0157	0.0092	0.0220	0.0236	0.0003	0.0016
Std Dev	0.0001	0.0002	0.0002	0.0001	0.0003	0.0002	0.0002	0.0002	<0.0001	0.0001
RSD	1.28	0.33	3.64	2.94	1.91	2.17	0.91	0.85	–	6.25
Std Avg	0.0162	0.0375	0.0045	0.0046	0.0264	0.0173	0.0176	0.0229	0.0072	0.0074
Std Acc	0.0012	0.0007	0.0008	0.0002	0.0020	0.0005	0.0005	0.0016	0.0002	0.0003
RSA	7.21	1.76	18.26	4.83	7.52	2.92	2.66	7.01	3.06	4.04
Maximum	0.0079	0.0600	0.0057	0.0035	0.0162	0.0096	0.0222	0.0239	0.0004	0.0018
Minimum	0.0077	0.0596	0.0052	0.0033	0.0155	0.0091	0.0217	0.0235	0.0003	0.0016
T	0.0002	0.0004	0.0005	0.0002	0.0007	0.0005	0.0005	0.0004	0.0001	0.0002
W	0.0010	0.0013	0.0011	0.0005	0.0013	0.0013	0.0009	0.0009	0.0002	0.0003

X4. EXAMPLE 4 TO ILLUSTRATE THIS PROCEDURE

X4.1 *Explanation of Need for Application of This Practice*—A reference material producer commissioned a local foundry to produce a lot of ductile iron chill cast specimens. The foundry cast part of a ductile iron heat into a series of five proprietary molds. Each mold produced a five by seven array of double chill cast cylinders. The specimens were double chilled because they were chilled from both ends. Each specimen was approximately 34 mm in diameter and 22 mm in thickness. The specimens were produced in the mold using a bottom pour, center feed, technique. Each cylinder was formed in a sand mold with copper chill blocks on each end. For each specimen, two chill fronts collided to produce a sample that was chilled throughout its entire length.

X4.1.1 The individual pieces were produced by removing the five by seven arrays from the molds, cutting the pieces out of the array, and removing lugs and flashings.

X4.1.2 The prepared pieces were delivered to the reference material producer for testing and preparation for interlaboratory, pre-certification, testing.

X4.1.3 The intent was to produce a Certified Reference Material (CRM) for the cast iron industry. CRM's must be uniform and well defined. The former requires homogeneity testing.

X4.2 *Preliminary Lot Processing*—The molds were designated T, U, V, W, and X.

X4.2.1 Mold and position were identifiable by stenciled letters and numbers in the copper blocks on one side of each piece.

X4.2.2 Mold U suffered a severe underfill problem, rendering its pieces unusable.

X4.2.3 Physical examination of the remaining 140 pieces indicated some possible losses due to cracking.

X4.2.4 The 140 pieces were labeled 1–140 (T1 = 1, T2 = 2, ... , X34 = 139, X35 = 140).

X4.3 *Within-Unit Homogeneity Testing*—Pieces 1, 18, 35, 36, 88, 105, 106, 122, and 140 were selected for within-unit homogeneity testing.

X4.3.1 A spreadsheet template was activated for the nine, dedicated to this case, and saved with the name of this application.

X4.3.2 The dedicated spreadsheet was configured to accommodate a 34 mm round sample. Seven locations were to be tested on one face of each sample (see Fig. X4.1). Spots 1–6 were to be around the circumference of the face. Spot 7 was to be in the middle of the face. The six peripheral spots were
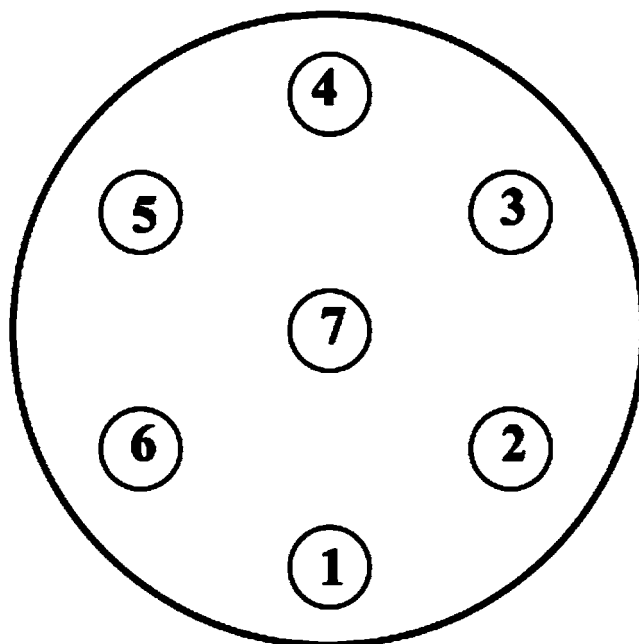

FIG. X4.1 Spot Placement on a Round Sample for Within-Unit Homogeneity Testing

sufficiently interior to the edges of each sample so as to assure a good seal on the plate of Spark-AES unit.

X4.3.3 The calibrant BS CI4 was selected as the drift monitor.

X4.3.4 A Spark-AES unit, which has been configured to produce reasonably stable output over long analytical runs, was prepared for the study.

X4.3.5 The drift monitor was burned at the beginning of each sequence, after the first group of four, and after the second group of three for a total of three determinations per sequence. Four runs were made for each sample for a total of 36 runs. Sequences were those given in the sequence chart generated by the dedicated spreadsheet (see Table X4.1).

X4.3.6 Determinations were captured in a database on the Spark-AES's hard drive.

X4.3.7 Upon completion of all determinations, the study data were extracted from the Spark-AES database and converted to a spreadsheet readable form.

X4.3.8 The study data were read into the dedicated spreadsheet and processed accordingly.

X4.3.9 Each spreadsheet template contains all generic information necessary for processing the data from a homogeneity study. The template is customized for the case under consideration and saved in its customized form. All actions associated with this practice are fully automated through the use of spreadsheet macros.

X4.3.10 For each sample the data were checked for proper burn position placement.

X4.3.11 For each element a significance test was performed. If the concentration or the overall relative standard deviation were too small, the element was discarded from the study.

X4.3.12 The data from the surviving elements were processed on an element by element basis.

X4.3.13 For the first element of the first sample (#1) the data from the four sequences were drift corrected, derandomized, and normalized in accordance with Sections 14 and 16, and presented to the analyst for examination.

X4.3.14 The analyst checked the presented data for proper placement (properly derandomized).

X4.3.15 The analyst authorized the spreadsheet to process the remaining elements of the first sample.

X4.3.16 The analyst processed the remaining eight samples in the same manner.

X4.3.17 When all pieces had been so processed, a final report was produced and printed. Two copies were produced: one for the analyst's records and one for the company records.

X4.4 *Between-Unit Homogeneity Testing*—Pieces 1, 18, 35, 36, 88, 105, 106, 122, and 140 were restored to the original collection of 140 and the entire group prepared for lot homogeneity testing.

X4.4.1 A spreadsheet template was activated for the group, dedicated to this case, and saved with the name of this application.

X4.4.2 The spreadsheet random function was used to select 15 specimens for the lot homogeneity check.

X4.4.3 The specimens selected were numbers: 9, 15, 33, 36, 45, 51, 65, 84, 99, 101, 104, 113, 127, 129, and 134.

X4.5 *Calibrant Selection*—Nine calibrants were selected for the composition phase of the homogeneity study, which was performed according to the procedure described in Section 17.

X4.5.1 These calibrants were: NIST 1140, NIST C2424, NIST C2425, BS 1C, BS 2C, BS 3C, BS 4C, BS 284, and BS 284C.

X4.5.2 BS 284 was selected as the drift monitor.

X4.6 *Data Generation*—A Spark-AES unit, which has been configured to produce reasonably stable output over long analytical runs, was prepared for the study.

X4.6.1 The determination sequence chart, produced by the dedicated spreadsheet, was utilized to guide the determination sequences for the study (see Table X4.2).

X4.6.2 Each determination was executed according to the determination sequence chart and the determinations captured in a database on the Spark-AES's hard drive.

X4.6.3 The drift monitor was run seven times in each determination sequence.

X4.6.4 Each calibrant/specimen array of 23 units was subdivided into five groups of four and one group of three.

X4.6.5 The drift monitor was run at the beginning of each sequence and after each grouping.

X4.7 *Data Processing*—Data from the study were extracted from the Spark-AES database and converted to a spreadsheet readable form.

X4.7.1 The study data were read into the spreadsheet and processed accordingly.

X4.7.2 The spreadsheet template contains all generic information necessary for processing the data from a homogeneity study. The template is customized for the case under consideration and saved in its customized form. All actions associated with this practice are fully automated through the use of spreadsheet macros.

X4.7.3 The data from the study was processed on an element by element basis.

X4.7.4 For each element the data from the four sequences was drift corrected, derandomized, and normalized in accordance with Sections 14 and 16, and presented to the analyst for examination.

X4.7.5 The analyst checked the presented data for proper placement (properly derandomized).

X4.7.6 The analyst executed a least-squares fit and examined the results on a correlation chart. If indicated, a higher degree fit was selected.

X4.7.7 The fit coefficients were applied to the specimens and a statistical report presented to the analyst for examination.

TABLE X4.1 Determination Sequence Chart for Within-Unit Homogeneity Testing (Round)

Monitor = BS CI4											
#1						**#18**					
Position	Burn	Run 1	Run 2	Run 3	Run 4	Position	Burn	Run 1	Run 2	Run 3	Run 4
Monitor	1	-1	-1	-1	-1	Monitor	1	-1	-1	-1	-1
#1	2	3	5	4	4	#1	2	3	5	4	4
#2	3	5	6	6	3	#2	3	5	6	6	3
#3	4	2	1	7	2	#3	4	2	1	7	2
#4	5	6	2	3	5	#4	5	6	2	3	5
Monitor	6	-1	-1	-1	-1	Monitor	6	-1	-1	-1	-1
#5	7	7	3	5	6	#5	7	7	3	5	6
#6	8	4	4	2	1	#6	8	4	4	2	1
#7	9	1	7	1	7	#7	9	1	7	1	7
Monitor	10	-1	-1	-1	-1	Monitor	10	-1	-1	-1	-1
#35						**#36**					
Position	Burn	Run 1	Run 2	Run 3	Run 4	Position	Burn	Run 1	Run 2	Run 3	Run 4
Monitor	1	-1	-1	-1	-1	Monitor	1	-1	-1	-1	-1
#1	2	3	5	4	4	#1	2	3	5	4	4
#2	3	5	6	6	3	#2	3	5	6	6	3
#3	4	2	1	7	2	#3	4	2	1	7	2
#4	5	6	2	3	5	#4	5	6	2	3	5
Monitor	6	-1	-1	-1	-1	Monitor	6	-1	-1	-1	-1
#5	7	7	3	5	6	#5	7	7	3	5	6
#6	8	4	4	2	1	#6	8	4	4	2	1
#7	9	1	7	1	7	#7	9	1	7	1	7
Monitor	10	-1	-1	-1	-1	Monitor	10	-1	-1	-1	-1
#88						**#105**					
Position	Burn	Run 1	Run 2	Run 3	Run 4	Position	Burn	Run 1	Run 2	Run 3	Run 4
Monitor	1	-1	-1	-1	-1	Monitor	1	-1	-1	-1	-1
#1	2	3	5	4	4	#1	2	3	5	4	4
#2	3	5	6	6	3	#2	3	5	6	6	3
#3	4	2	1	7	2	#3	4	2	1	7	2
#4	5	6	2	3	5	#4	5	6	2	3	5
Monitor	6	-1	-1	-1	-1	Monitor	6	-1	-1	-1	-1
#5	7	7	3	5	6	#5	7	7	3	5	6
#6	8	4	4	2	1	#6	8	4	4	2	1
#7	9	1	7	1	7	#7	9	1	7	1	7
Monitor	10	-1	-1	-1	-1	Monitor	10	-1	-1	-1	-1
#106						**#122**					
Position	Burn	Run 1	Run 2	Run 3	Run 4	Position	Burn	Run 1	Run 2	Run 3	Run 4
Monitor	1	-1	-1	-1	-1	Monitor	1	-1	-1	-1	-1
#1	2	3	5	4	4	#1	2	3	5	4	4
#2	3	5	6	6	3	#2	3	5	6	6	3
#3	4	2	1	7	2	#3	4	2	1	7	2
#4	5	6	2	3	5	#4	5	6	2	3	5
Monitor	6	-1	-1	-1	-1	Monitor	6	-1	-1	-1	-1
#5	7	7	3	5	6	#5	7	7	3	5	6
#6	8	4	4	2	1	#6	8	4	4	2	1
#7	9	1	7	1	7	#7	9	1	7	1	7
Monitor	10	-1	-1	-1	-1	Monitor	10	-1	-1	-1	-1
#140											
Position	Burn	Run 1	Run 2	Run 3	Run 4						
Monitor	1	-1	-1	-1	-1						
#1	2	3	5	4	4						
#2	3	5	6	6	3						
#3	4	2	1	7	2						
#4	5	6	2	3	5						
Monitor	6	-1	-1	-1	-1						
#5	7	7	3	5	6						
#6	8	4	4	2	1						
#7	9	1	7	1	7						
Monitor	10	-1	-1	-1	-1						

X4.7.8 When all elements had been so processed, a final report was produced and printed (see Table X4.3). Two copies were produced: one for the analyst's records and one for the company records.

X4.8 *Depth Homogeneity Study*—The nature of chill cast iron is such that some degree of graphitization can occur at any depth in a piece. This is especially true for single face chill cast pieces. It is vital to determine whether this has occurred and if

TABLE X4.2 Determination Sequence Chart for Between-Unit Homogeneity Testing

Sample	Burn	Run 1	Run 2	Run 3	Run 4
		Monitor = BS 284			
Monitor	1	M	M	M	M
NIST 1140	2	12	14	5	20
NIST C2424	3	17	6	22	9
NIST C2425	4	21	22	17	17
BS 1C	5	14	11	19	8
Monitor	6	M	M	M	M
BS 2C	7	20	1	16	23
BS 3C	8	9	7	13	21
BS 4C	9	15	3	2	4
BS 284C	10	13	5	6	10
Monitor	11	M	M	M	M
#9	12	16	16	10	13
#15	13	19	10	4	16
#33	14	3	18	21	19
#36	15	23	9	1	15
Monitor	16	M	M	M	M
#45	17	2	15	11	3
#51	18	18	21	7	12
#65	19	5	13	12	6
#84	20	11	4	14	18
Monitor	21	M	M	M	M
#99	22	10	19	9	5
#101	23	7	12	3	22
#104	24	6	20	15	7
#113	25	8	8	8	11
Monitor	26	M	M	M	M
#127	27	4	2	20	2
#129	28	22	23	18	14
#134	29	1	17	23	1
Monitor	30	M	M	M	M

TABLE X4.3 Lot Report—For Some Elements

Sample	C	Mn	P	S	Si	Cu	Ni	Cr	V
#9	3.02	0.275	0.0211	0.0102	0.891	0.069	0.048	0.073	0.0077
#15	3.03	0.274	0.0204	0.0105	0.893	0.066	0.048	0.073	0.0077
#33	3.02	0.276	0.0210	0.0096	0.890	0.065	0.048	0.073	0.0077
#36	3.01	0.275	0.0209	0.0106	0.890	0.070	0.048	0.074	0.0077
#45	3.00	0.274	0.0209	0.0111	0.894	0.070	0.048	0.073	0.0076
#51	2.99	0.274	0.0209	0.0099	0.892	0.065	0.048	0.073	0.0076
#65	3.01	0.276	0.0207	0.0107	0.892	0.069	0.048	0.073	0.0077
#84	3.00	0.276	0.0205	0.0098	0.902	0.067	0.048	0.073	0.0077
#99	3.01	0.273	0.0209	0.0109	0.895	0.077	0.048	0.073	0.0076
#101	3.03	0.277	0.0210	0.0099	0.890	0.066	0.048	0.074	0.0077
#104	3.00	0.276	0.0205	0.0098	0.888	0.069	0.048	0.074	0.0077
#113	3.00	0.274	0.0209	0.0100	0.893	0.069	0.048	0.073	0.0075
#127	3.00	0.274	0.0204	0.0114	0.891	0.065	0.048	0.073	0.0076
#129	3.02	0.276	0.0206	0.0105	0.889	0.066	0.048	0.074	0.0078
#134	3.03	0.276	0.0209	0.0103	0.897	0.071	0.048	0.073	0.0077
Avg	3.01	0.275	0.0208	0.0103	0.892	0.068	0.048	0.073	0.0077
Std Dev	0.01	0.001	0.0002	0.0005	0.004	0.003	0.000	0.000	<0.0001
RSD	0.33	0.36	0.96	4.85	0.45	4.69	0.42	0.55	–
Std Acc	0.04	0.011	0.0023	0.0031	0.058	0.012	0.011	0.002	0.0022
Maximum	3.03	0.277	0.0211	0.0114	0.902	0.076	0.048	0.074	0.0078
Minimum	2.99	0.273	0.0204	0.0096	0.888	0.064	0.048	0.072	0.0075
T	0.04	0.004	0.0007	0.0018	0.014	0.012	0.001	0.001	0.0003
W	0.06	0.005	0.0008	0.0029	0.021	0.012	0.002	0.001	0.0003

so, to what degree and depth.

X4.8.1 Precipitated graphite, or for that matter, any other nonmetallic inclusion, can "upset" the spark process in Spark-AES and render results questionable. That is, the Spark-AES can be phase sensitive.

X4.8.2 Previous testing had shown that apparent concentration gradients in chill cast pieces were due to graphite precipitation, not true gradients.

X4.8.3 Previous experience with this foundry and this material had shown that the introduction of certain inoculants would control this problem satisfactorily.

X4.8.4 It was, however, still necessary to verify apparent depth homogeneity.

X4.8.5 Piece #82 was selected for the depth study.

X4.8.6 The non-analytical face was planed with a swing grinder to a "clean metal" appearance. The analytical face was planed to a depth of 100 thousandths of an inch. Experience had shown that this was the optimum depth for the commencement of normal use.

X4.8.7 A series of within-unit like studies was performed as described in X4.3 (see Table X4.4). Instead of several pieces, successive layers were examined. Each layer was tested, a new layer exposed, and that layer tested. Layers were produced by planing off 100 thousandths each time with a swing grinder.

X4.8.8 Given that the analytical face described in X4.8.6 was the initial (0) layer, layers examined were: 0, -100, -200,

-300, -400, -500. It was unnecessary to proceed further as the remaining piece was too thin to handle safely and the "chill collision zone" had been passed.

X4.8.9 When all layers had been so processed, a final report was produced and printed (see Table X4.5). Two copies were produced: one for the analyst's records and one for the company records.

X4.9 *Preparation for Interlaboratory Study*—All hardcopy and electronic data was archived.

X4.9.1 All reports were filed and archived.

X4.9.2 Final compositional data were compiled as a guide to participants in the interlaboratory study.

X4.9.3 All pieces of the lot were processed to final, usable, form. Defective pieces were discarded.

X4.9.4 Pieces were reserved for participants requiring solid samples. Chips were produced for those requiring chip samples.

X4.9.5 Interlaboratory study participants were selected.

X4.9.6 Samples were sent to selected participants for analysis.

TABLE X4.4 Determination Sequence Chart for the Depth Study

Monitor = BS CI4											
0						-100					
Position	Burn	Run 1	Run 2	Run 3	Run 4	Position	Burn	Run 1	Run 2	Run 3	Run 4
Monitor	1	-1	-1	-1	-1	Monitor	1	-1	-1	-1	-1
#1	2	3	5	4	4	#1	2	3	5	4	4
#2	3	5	6	6	3	#2	3	5	6	6	3
#3	4	2	1	7	2	#3	4	2	1	7	2
#4	5	6	2	3	5	#4	5	6	2	3	5
Monitor	6	-1	-1	-1	-1	Monitor	6	-1	-1	-1	-1
#5	7	7	3	5	6	#5	7	7	3	5	6
#6	8	4	4	2	1	#6	8	4	4	2	1
#7	9	1	7	1	7	#7	9	1	7	1	7
Monitor	10	-1	-1	-1	-1	Monitor	10	-1	-1	-1	-1
-200						-300					
Position	Burn	Run 1	Run 2	Run 3	Run 4	Position	Burn	Run 1	Run 2	Run 3	Run 4
Monitor	1	-1	-1	-1	-1	Monitor	1	-1	-1	-1	-1
#1	2	3	5	4	4	#1	2	3	5	4	4
#2	3	5	6	6	3	#2	3	5	6	6	3
#3	4	2	1	7	2	#3	4	2	1	7	2
#4	5	6	2	3	5	#4	5	6	2	3	5
Monitor	6	-1	-1	-1	-1	Monitor	6	-1	-1	-1	-1
#5	7	7	3	5	6	#5	7	7	3	5	6
#6	8	4	4	2	1	#6	8	4	4	2	1
#7	9	1	7	1	7	#7	9	1	7	1	7
Monitor	10	-1	-1	-1	-1	Monitor	10	-1	-1	-1	-1
-400						-500					
Position	Burn	Run 1	Run 2	Run 3	Run 4	Position	Burn	Run 1	Run 2	Run 3	Run 4
Monitor	1	-1	-1	-1	-1	Monitor	1	-1	-1	-1	-1
#1	2	3	5	4	4	#1	2	3	5	4	4
#2	3	5	6	6	3	#2	3	5	6	6	3
#3	4	2	1	7	2	#3	4	2	1	7	2
#4	5	6	2	3	5	#4	5	6	2	3	5
Monitor	6	-1	-1	-1	-1	Monitor	6	-1	-1	-1	-1
#5	7	7	3	5	6	#5	7	7	3	5	6
#6	8	4	4	2	1	#6	8	4	4	2	1
#7	9	1	7	1	7	#7	9	1	7	1	7
Monitor	10	-1	-1	-1	-1	Monitor	10	-1	-1	-1	-1

TABLE X4.5 Partial Depth Study Report

NOTE 1—The exclamation point indicates the results are reported in ppm.

	C	Mn	P	S	Si	Cu	Ca!	Mg!
	#82 (W-12) – 200 Thousandths							
Circ 1	3.04	0.268	0.0226	0.0087	0.871	0.0731	14	400
Circ 2	3.01	0.269	0.0217	0.0096	0.875	0.0664	16	405
Circ 3	3.02	0.267	0.0213	0.0090	0.874	0.0645	15	392
Circ 4	3.02	0.267	0.0214	0.0094	0.884	0.0695	17	410
Circ 5	3.02	0.266	0.0215	0.0094	0.870	0.0661	17	402
Circ 6	3.03	0.266	0.0218	0.0084	0.862	0.0673	13	386
Middle	3.04	0.267	0.0213	0.0095	0.865	0.0677	21	395
Avg	3.02	0.267	0.0217	0.0091	0.871	0.0678	16	399
Std Dev	0.01	<0.001	0.0005	0.0004	0.007	0.0028	3	8
RSD	0.33	–	2.3	4.4	0.80	4.13	15.72	2.03
Maximum	3.04	0.269	0.0226	0.0096	0.884	0.0731	21	410
Minimum	3.01	0.266	0.0213	0.0084	0.862	0.0645	13	386
T	0.03	0.003	0.0013	0.0012	0.022	0.0086	7	24
W	0.07	0.006	0.0016	0.0027	0.023	0.0154	9	28

X5. ADDITIONAL INFORMATION CONCERNING THE USE OF TABLE 1 FOR STATISTICAL ANALYSIS OF DATA

X5.1 It is often desirable in some solid specimens to examine the homogeneity from front to back, corner-to-corner, etc. to find compositional differences caused by metallurgical structure or segregation. This statistical procedure allows one to obtain such information. For example, to determine if there is a significant difference between the front and back sides of a solid disk specimen, the two sides of the one specimen are treated as though they were two separate specimens. Then the data in Tables X1.3 and X1.4 would reflect the difference between the sides of the specimen. To ensure that the sides of the specimen are taken at random for measurement, the following sequence is recommended:

	Specimen	
↓ Side	A	B
a	1	3
b	4	2

X5.1.1 That is, for two specimens A and B, each having sides a and b, the recommended sequence is aA, bB, aB, bA.

X5.2 The recommended sequences for three to six specimens are given in Table X5.1.

TABLE X5.1 Recommended Sequences for Three to Six Specimens

Side	Specimens					
	A	B	C	D	E	F
a	1	5	4	...	...	...
b	6	2	3	...	...	...
a	1	7	6	4	...	...
b	8	2	3	5	...	...
a	1	8	9	5	4	...
b	10	3	2	6	7	...
a	1	11	3	9	8	7
b	12	2	10	4	5	6

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