~~Designation:E826–85 (Reapproved 1996)$^{\epsilon 1}$~~ Designation: E 826 – 08

Standard Practice for ~~Testing Homogeneity of Materials for Development of Reference Materials~~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 E 826; 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.

~~ϵ^1 NOTE—Section 12 was added editorially in June 1996.~~

1. Scope

~~1.1This practice is suitable for testing the homogeneity of metals, either in solid or powdered form, and finely ground oxide materials that are intended for use as reference materials in X-ray emission, or optical emission spectroscopy, or both. The criteria for acceptance of the test specimens as reference materials, however, must be previously determined by the user for meeting his specific requirements.~~

~~1.2The procedure is designed primarily for testing specimens by X-ray emission spectrometry or optical emission spectroscopy, or both. However, the practice could be easily adapted for use with other instrumental techniques such as atomic absorption spectrophotometry.~~

~~1.3This procedure can be applied to one or more elements in a specimen provided the signal-to-background ratio is not a limiting factor.~~

~~1.4This practice includes one method, if desired, to correct for systematic or periodic (sinusoidal) drift in the instrument with time through the use of a control reference material.~~

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).

~~NOTE1—**Caution:** If serious drift occurs (for example, unstable power supply, X-ray tube, etc.) erroneous conclusions may be obtained from the data analysis.~~

~~1.5~~ *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] This practice is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.22 on Statistics and Quality Control.~~

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

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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]

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

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E 178 Practice for Dealing ~~with~~With Outlying Observations

E~~876Practice for Use of Statistics in the Evaluation of Spectrometric Data~~ 634 Practice for Sampling of Zinc and Zinc Alloys for Optical Emission Spectrometric Analysis

E 716 Practices for Sampling Aluminum and Aluminum Alloys for Spectrochemical Analysis

E 1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E 1806 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 E 135~~, and Practices E177 and E178~~, and Practices E 177, E 178, E 1329, and E 1806.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 ~~*drift*—a gradual systematic or sinusoidal change in instrument readings with time.~~ 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*, is statistically acceptable differences among means of specimens in the test. —*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 E 1806.

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

~~4.1This procedure, which is based on statistical methods (**1-6**), consists of stepwise instructions for testing homogeneity of candidate reference materials. The candidate materials are selected as described in Section 6, and then measured by either X-ray emission or optical emission spectroscopy (see Sections 7 and 8). The resultant data are corrected for instrumental drift, if desired (see Section~~

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 tabulated (see Table 1, Table X1.3, and Table X1.4) to facilitate the statistical calculations that are performed according to Section 9. The homogeneity of the material is determined from the results of the data analysis.~~

~~4.2This procedure *requires* that repeated measurements on the same specimen have sufficient precision (that is, repeatability) through appropriate selection of instrumental parameters so that any significant difference among specimens can be detected with confidence.~~

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* ~~, Vol 03.05.~~volume information, refer to the standard's Document Summary page on the ASTM website.

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

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

~~[4] Annual Book of ASTM Standards, Vol 03.06.~~

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

TABLE 1 Data for Homogeneity Testing[A]

RunNo.	SpecimenNumber							Total				
	146	296	385	4	5 ...77		...*t*[A]27		928626	4521	89	91	714264
1								B_{33}	29450031 = 34		84	05	729044
	44	19	15	32	63	55	87	77	33	294500	3134	84	05	729044
2								$B_{2=8}$	113479	2635	34	23	099400
	34	39	80	62	24	33	81	67	28	113479	2635	34	23	099400
3								B_{01}	844745	8970	7413 =		049051
	74	97	80	30	65	07	71	30	01	844745	8970	74	13	049051
4								B_{13}	337208	1613	50	564 =	851294
	22	14	61	60	86	38	33	71	13	337208	1613	50	56	485129
5...								B_{09}	212118	0005... =	86	52	854073
	40	03	96	40	03	47	24	60	09	212118	0005	86	52	854073
...*b*[B]								$B_n = 78$	737819	8706	98	47	480262
	52	33	76	44	56	15	47	75	78	737819	8706	98	47	480262
Total	$T_1 =$	$T_{2=}$	$T_3 =$	$T_4 =$	$T_5 =$	...	$T_n =$	$G = (\Sigma B_{1...B_n})9$	908087	3274	59	84	244979
	37	59	20	40	93	17	82	24	19	908087	3274	59	84	244979
Mean	$t'_1 =$	$t'_2 =$	$t'_3 =$	$t'_{4=}$	$t'_5 =$	...	$t'_n =$		22	671920	1592	53	37	137554
	11	02	55	57	48	84	74	36	22	671920	1592	53	37	137554
	10	33	79	26	34	54	71	33	89	746848	2317	49	18	810552
	67	59	28	25	47	89	11	65	65	204223	9641	64	20	308987
	93	50	75	20	09	18	54	34	68	025487	2305	43	36	982997
	24	43	23	72	80	64	34	27	23	461536	1063	21	59	697602
	39	91	63	18	38	27	10	78	88	844232	0097	92	00	049450
	74	62	19	67	54	18	28	92	33	699896	7435	72	11	682508
	91	03	35	60	81	16	61	97	25	147821	2205	25	47	263780
	42	57	66	76	72	91	03	63	48	464401	3353	62	28	805955
	06	36	63	06	15	03	72	38	01	582537	6648	56	19	564129
	92	70	96	70	89	80	87	14	25	492594	6278	26	15	413948
	91	08	88	53	52	13	04	82	23	002636	4744	04	08	848007
	68	85	97	74	47	53	90	05	90	848748	2501	11	05	451143
	59	54	13	09	13	80	42	29	63	032464	1243	28	10	016562
	39	18	32	69	33	46	58	19	34	035928	9731	02	65	474770
	67	43	31	09	12	60	19	57	63	781180	1097	15	70	048981
	61	75	37	19	56	90	75	39	03	564992	7295	27	52	874712
	78	10	91	11	00	63	19	63	74	586903	5138	60	36	535677
	93	23	71	58	09	78	08	03	07	717932	2519	61	04	403312
	37	55	48	82	63	89	92	59	14	721917	2251	90	20	036496
	62	13	11	71	17	23	29	25	13	853335	0769	25	68	579257
	29	89	97	47	03	13	20	86	22	455998	6453	89	64	948155
	16	94	85	82	89	07	17	30	29	898980	9836	25	36	530249
	04	93	10	59	75	12	98	84	60	936816	8760	11	50	465658
	95	71	43	68	97	18	85	17	13	080050	7750	46	92	452697
	86	05	39	14	35	48	68	18	36	570962	4028	87	08	747991
	59	30	60	10	41	31	00	69	63	770189	9460	19	02	708872
	05	45	35	40	54	03	98	96	76	277784	8008	64	60	443454
	71	85	17	74	66	27	85	19	55	565136	4892	32	44	404710
	80	20	32	80	98	00	40	92	57	515283	1455	31	99	732340
	13	50	78	02	73	39	66	82	01	286751	7566	33	97	475842
	67	92	65	41	45	36	77	96	46	211439	5636	70	15	744362
	72	56	73	44	26	04	62	81	15	357926	9957	28	22	259480
	28	86	85	64	94	11	58	78	45	363445	9138	51	10	683687
	69	57	40	80	44	94	60	82	94	939801	4850	57	69	607769
	71	20	03	30	79	25	74	17	78	345445	0477	42	59	757864
	89	98	55	98	22	45	12	49	82	715733	2869	50	59	150925
	58	74	82	81	14	02	01	05	77	946557	7039	42	48	568431
	50	54	73	81	91	07	81	26	25	454961	2288	41	20	001559
	49	33	72	90	10	20	65	28	44	639586	7578	69	24	416586
	11	85	01	43	65	02	85	69	56	883429	6435	48	15	701177
	34	22	46	41	84	74	27	02	57	774793	7202	95	63	757469

[A] *A Million Digits*=numby The Rand Corpof sration, Copeeyrimght, Thens.
[B] *b*=numb Free Pr-of runess, 1955.

4.3This procedure requires that there be an absence of outliers in the data (see Practice E178).

NOTE2—**Caution:**, 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 E 1329), normalization, and drift monitoring.

4.4 This practice requires that there be an absence of outliers in the data (Practice E 178). (**Warning—** The use of Practice E 178 ~~dealing with outliers should be done with extreme care to ensure that values are not discarded that may be valid for the analysis.~~ 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

~~5.1The purpose of this practice is to ensure the quality of materials selected in order that they can serve as a supplement to primary standard reference materials.~~

~~5.2This procedure 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.~~

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. ~~Selection of Test Specimens from a Large Batch~~

~~6.1If the candidate material consists of 15 specimens or less, then all specimens should be tested.~~

~~6.2If the candidate material is in a form or quantity that prohibits testing all specimens, then a minimum of 8% but not less than 15 specimens shall be tested according to the random sample selection scheme described in 6.3~~Summary of the Test Method

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

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

where:

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

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

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

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 E 1601), 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 corresponds to zero height. Further, suppose the axis of the cylinder defines the origin of an XYZ coordinate system. The *z* axis corresponds to the cylinder axis. The *x* and *y* axes can be oriented as one chooses. Let the *x* axis correspond to an angle of zero degrees. Then, every point in the cylinder can be described by its height from the plane ($H \geq Z$), its distance from the central axis (R), and its angle with respect to the *x* axis (Θ).

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

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

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

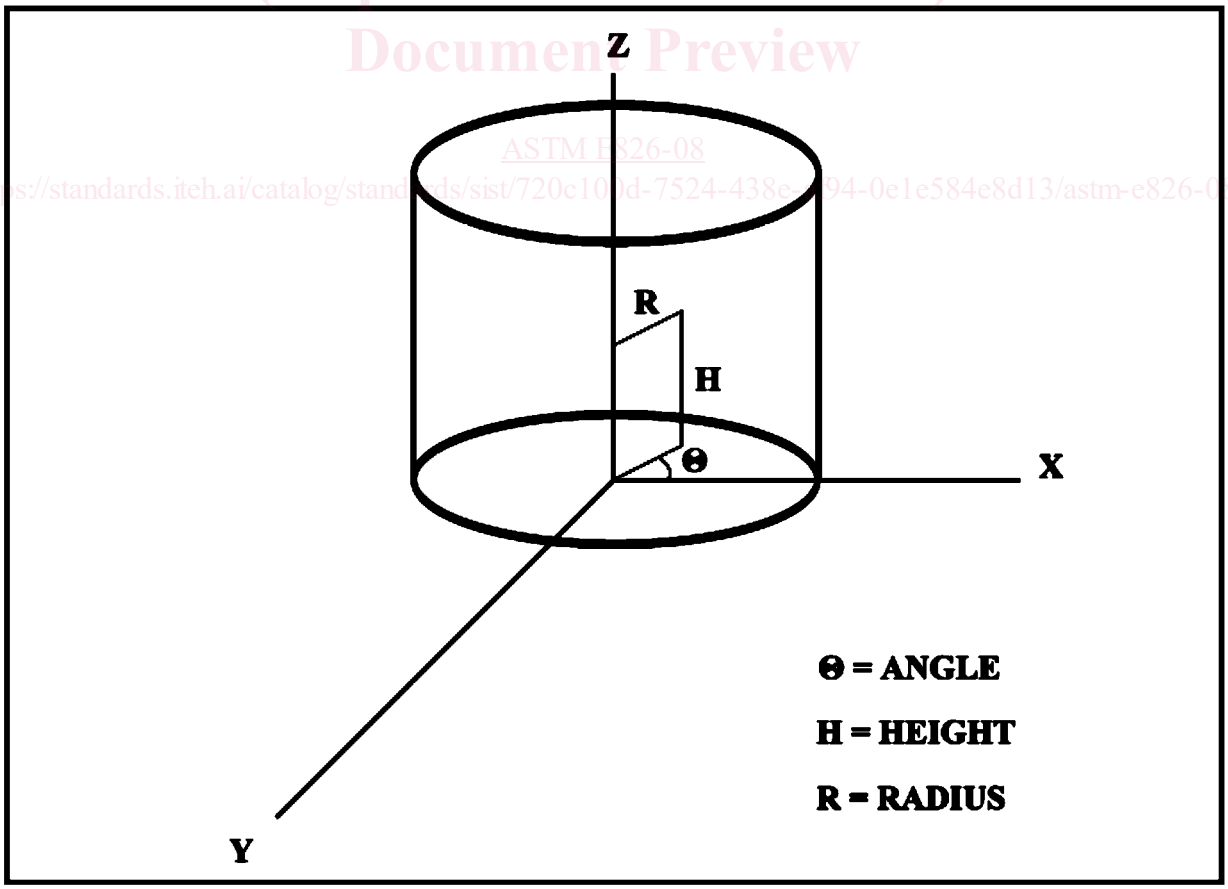

FIG. 1

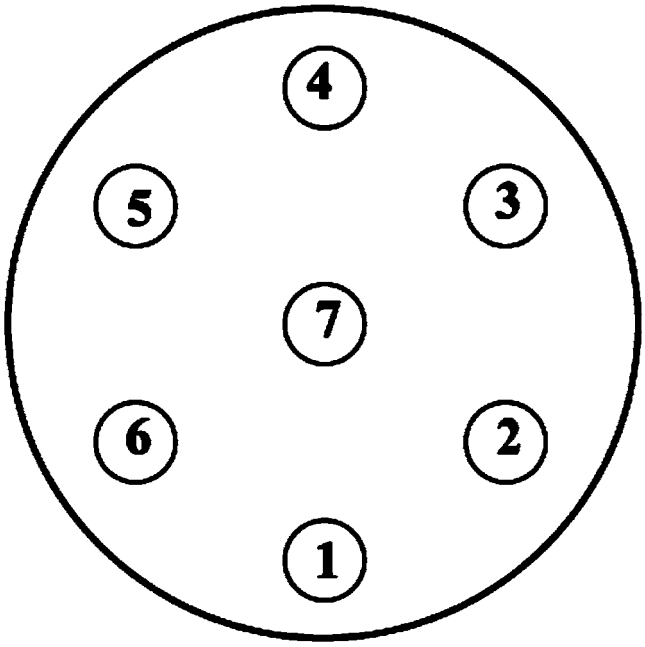

FIG. 2

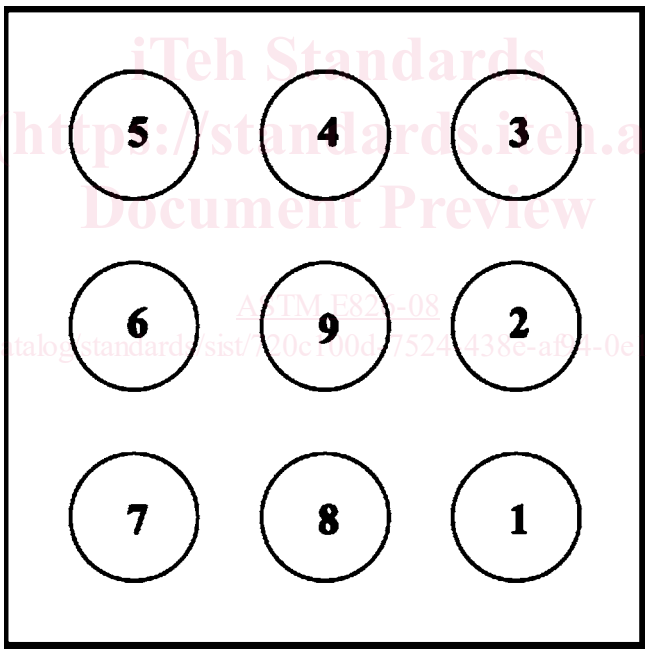

FIG. 3

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 *i*th randomly chosen position and n is the total number of positions. Four such sequences are run. The resultant data are derandomized and presented as a 4 × n matrix. The resultant matrix is processed in accordance with Section 12.

~~6.3Label all specimens consecutively (that is, 01, 02, 03,···). From a table of random numbers~~

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

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

8.3 *Within-Unit Homogeneity (Z)*—For alloys known or suspected to be heterogeneous as a function of depth, it may be

necessary to slice each piece at one or more distances from the original face to create test portions for (R, Θ) testing. An alternative would be to measure both faces of each piece (where practical). Another alternative would be to remove successive layers of material and test each layer so produced. This sub-sampling should be designed to allow the analyst to make a statement about the depth to which the material is to be certified for use.

8.4 *Between-Unit Homogeneity (Contiguous)*—This case occurs for ingots or bar stock. It is assumed that enough samples have been processed or enough is known about the production method so as to assure the analyst that the ingot or bar is homogeneous with respect to (R, Θ). Procure specimens representative of both ends and the middle. For each of the end pieces use the inside face for analysis. For the middle piece either face will suffice. Surface all pieces in the normal manner. Burn each piece in random order. Burn a new random sequence. Repeat until four sequences have been burned. The resultant data are derandomized and presented as a 4 × 3 matrix. The resultant matrix is processed in accordance with Section 12.

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

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

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

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

9. The Test Portion

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

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

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

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

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

10. Selection of Test Specimens

10.1 Practices E 634, E 716, and E 1806 are currently the only standards that provide procedures for sampling metals. As such, they only apply to aluminum, iron, and zinc alloys. However, the analyst may use them as guidelines for sampling other metal alloys.

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

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

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

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

10.6 A completely random selection of specimens can be accomplished by labeling all specimens consecutively (that is, 01, 02, 03, ...) and using a table of random numbers to select individual specimens. From a table of random numbers **(3)** ~~(see Table 2 and Note 3), 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. Select those specimens for testing which match the numbers read from the tables.~~) (see Table 1 and Note 7), pick an arbitrary starting place and select any direction for reading the numbers, provided the direction is fixed in advance and is independent of the numbers occurring. As an alternative, a computer generated list can be used such as would be found in a random number generator (spreadsheet based or otherwise).

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

NOTE 3—~~**Caution:**~~ 7—Table ~~2~~1 included herein is for example, only. Use the more complete tables in Ref **(3)** ~~when actually using this test procedure.~~

~~**7.X-Ray Emission Spectroscopy Test Procedure**~~

~~7.1Select optimum instrumental conditions to assure adequate count rates from each element to be tested in the specimens.~~

~~7.2Select a counting time that is long enough to minimize the random error due to counting. Also, avoid counting rates greater than 70000 c/s to minimize dead-time corrections in the detection system.~~

~~7.3Measure the element(s) of interest on the specimens selected in Section 6. Repeat the measurements of X-ray intensity until a minimum of four sets have been made. For each set, the specimens shall be taken in random order.~~

~~7.4If correction of instrumental drift is desired, a control reference material shall be measured along with the specimens.~~

~~7.5Examine the data and discard any values which have been determined to be outliers according to Practice E178. In Table 1, enter either the raw or normalized values for each element, or values corrected for drift.~~

~~7.6If any outliers occur, repeat the complete test, as provision is not made for missing data in the mathematical treatment.~~

~~**8.Optical Emission Spectroscopy Test Procedure**~~

~~8.1Select optimum instrumental conditions to obtain adequate sensitivity for each element to be tested in the specimens.~~

~~8.2Use excitation conditions appropriate for the element(s) of interest. Select a spectral line(s) that has a minimum of interferences from other elements in the specimen.~~

~~8.3Measure the element(s) of interest in the specimens selected in Section 6. Repeat the measurements until a minimum of four sets have been made. For each set, take the specimens in random order.~~

~~8.4If correction of instrumental drift is desired, measure a control reference material along with the specimens. The control reference material shall be homogeneous with respect to the element(s) being determined, in the specimens.~~

~~8.5Examine the data and discard any values that have been determined to be outliers according to Practice E178. In Table 1, enter either the raw or normalized values for each element or values corrected for drift.~~

~~8.6If any outliers occur, repeat the complete test, as provision is not made for missing data in the mathematical treatment.~~

~~**9.Calculations to Determine Homogeneity**~~

~~9.1Compute *T, B, t′,* and *G*, (see Table 1), where: *T*=sum of each column; *B*=sum of each row; *t′*=mean of each column; and *G*=sum of $B_1 \cdots B_n$; *b=number of replicate measurements (that is, runs); and t=number of specimens.*~~

~~9.2Choose a significance level (α) for the test.~~ *) 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.

TABLE 2 4 Short Table of Random Numbers $R = S_1^2/S_2^2$ Ratio[A] Note 1—Caution: See Note 3 Note 3.

46 Number of Measurements (n) on Monitor	96																							18 Ratio
4 4	19	15	32	63	55	87	77	33	29	45	00	31	34	84	05	72	90	44	27	78	22	07	62	17	
4	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	
5	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	
6	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	
7	14	61	60	86	38	33	71	13	33	72	08	16	13	50	56	48	51	2.94	48	30	93	45	66	29	
8	0.98																								
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	
9	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	
10	33	79	26	34	54	71	33	89	74	68	48	23	17	49	18	81	.05	52	85	70	05	73	11	76	
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	
67	59	28	25	47	89	11	65	65	20	42	23	96	41	64	2.10	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	
59	54	13	09	13	80	42	29	63	03	24	64	12	43	28	10	0.16	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	
67	43	31	09	12	60	19	57	63	78	11	80	10	97	15	70	04	89	81	78	54	84	87	83	4.21	
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	
37	55	48	82	63	89	92	59	14	72	19	17	22	51	90	20	1.36	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	
62	13	11	71	17	23	29	25	1.38	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	

[A] Reprinted with permission from A Million Digits 3 by T) is she Rown as and C example. For p mora tie con mplete tables, C see (3 and 4). Ho pywevering, the values in t, The F latter refe Prences are half the values, 1955 shown in this table because of a slightly different method of determination.

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.

TABLE 3 2 Values of ~~*q* for Various Combinations of *t* and *ν* at 95% Significance Level (1)~~

~~ν~~Position or ↓	Specimen →	Burn Number															
	1	2	3	4	~~5~~...	~~6~~*b*	~~7~~T		~~8~~T^2	~~9~~X^2	~~10~~t'						
	~~1~~	~~17.97~~	~~26.98~~	~~32.82~~	~~37.08~~	~~40.41~~	~~43.12~~	~~45.40~~		~~47.36~~	~~49.07~~						
1	x_{11}	x_{12}	x_{13}	x_{14}	...	x_{1b}	T_{1}~~2~~	~~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~~						
	$2x_{1j}$	T_1^2	~~8.33~~	~~9.80~~	X~~10.88~~	~~11.74~~	~~12.44~~	~~13.03~~		~~13.54~~	~~13.99~~						
	3	~~4.50~~	~~5.9~~*16.82*	~~7.50~~	~~8.04~~	~~8.48~~	~~8.85~~	~~9.18~~		~~9.46~~							
	$3x_{1j}^2$	~~4.50~~	~~5.9~~$\bar{t}_{16.82}$	~~7.50~~	~~8.04~~	~~8.48~~	~~8.85~~	~~9.18~~		~~9.46~~							
	~~4~~3.93	~~5.04~~	~~5.76~~	~~6.29~~	~~6.7~~$_{17.05}$	~~7.35~~	~~7.60~~	~~7.83~~									
	~~4~~3.93	~~5.04~~	~~5.76~~	~~6.29~~	~~6.7~~$_{17.05}$	~~7.35~~	~~7.60~~	~~7.83~~/b									
	~~5~~	~~3.64~~	~~4.60~~	~~5.22~~	~~5.67~~	~~6.03~~	~~6.33~~	~~6.58~~		~~6.80~~	~~6.99~~						
2	x_{21}	x_{22}	x_{23}	x_{24}	...	x_{2b}	~~6.33~~	~~6.58~~		~~6.80~~	~~6.99~~						
	~~6~~	3.46	~~4.34~~	~~4.90~~	~~5.30~~	~~5.63~~	~~5.90~~	~~6.1~~*26.32*~~6.49~~									
	T_2 ~~6~~x_{2j}	T_2^2	~~4.34~~	~~4.90~~	~~5.30~~	~~5.63~~	~~5.90~~	~~6.1~~X~~22~~6.49									
	7	~~3.34~~	~~4.16~~	~~4.68~~	~~5.06~~	~~5.36~~	~~5.61~~	~~5.8~~*26.00*		~~6.16~~							
	~~7~~x_{2j}^2	~~3.34~~	~~4.16~~	~~4.68~~	~~5.06~~	~~5.36~~	~~5.61~~	~~5.8~~$\bar{t}_{26.00}$		~~6.16~~							
	~~83.~~$_{26}$	~~4.04~~	~~4.53~~	~~4.89~~	~~5.17~~	~~5.40~~	~~5.60~~	~~5.77~~		~~5.92~~							
	~~8~~$_{26}$	~~4.04~~	~~4.53~~	~~4.89~~	~~5.17~~	~~5.40~~	~~5.60~~	~~5.77~~		~~5.92~~/b							
	~~9~~	~~3.20~~	~~3.95~~	~~4.41~~	~~4.76~~	~~5.02~~	~~5.24~~	~~5.4~~*35.59*		~~5.74~~							
3	x_{31}	x_{32}	x_{33}	x_{34}	...	x_{3b}	~~5.24~~	~~5.4~~$T_{35.59}$		~~5.74~~							
	10	~~3.15~~	~~3.88~~	~~4.33~~	~~4.65~~	~~4.91~~	~~5.1~~25.30	~~5.46~~		~~5.60~~							
	10x_{3j}	T_3^2	X~~3.88~~	~~4.33~~	~~4.65~~	~~4.91~~	~~5.1~~25.30	~~5.46~~		~~5.60~~							
	11	~~3.11~~	~~3.82~~	~~4.26~~	~~4.57~~	~~4.82~~	~~5.03~~	~~5.20~~		~~5.35~~	~~5.49~~						
	11x_{3j}^2	$\bar{t}_{3.11}$	~~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~~							
	12$_{3.08}$	~~3.77~~	~~4.20~~	~~4.51~~	~~4.75~~	~~4.95~~	~~5.12~~	~~5.27~~		~~5.39~~/b							
	~~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~~
t	x_{t1}	x_{t2}	x_{t3}	x_{t4}	...	x_{tb}	T_{t} 16x_{tj}		T_t^2	~~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~~						
	X_t^2 17x_{tj}^2	~~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~~							
	t_t 18~~2.97~~	~~3.61~~	~~4.00~~	~~4.28~~	~~4.49~~	~~4.67~~	~~4.82~~	~~4.96~~		~~5.07~~$_t$/b							
	~~19~~	~~2.96~~	~~3.59~~	~~3.98~~	~~4.25~~	~~4.47~~	~~4.65~~	~~4.79~~		~~4.92~~	~~5.04~~						
B	B_1 19x_{i1}	$B_{2.96}$	~~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~~						
	20x_{i2}	~~2.95~~	$B_{3.58}$	~~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~~						
	24x_{i3}	~~2.92~~	~~3.53~~	~~3.90~~	$B_{4.17}$	~~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~~						
	30x_{i4}	...	~~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~~							
	B_b 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~~x_{ib}							
	~~120~~	~~2.80~~	~~3.36~~	~~3.68~~	~~3.92~~	~~4.10~~	~~4.24~~	~~4.36~~		~~4.47~~			$G = \Sigma T_j$		~~4.56~~		
B^2	B_1^2	B_2^2	B_3^2	B_4^2	...	Bb~~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~~						

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

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

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

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

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

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

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

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

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

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

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

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

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

11.14 Examine the data and discard any values that have been determined to be outliers according to Practice E 178. 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~~4—A 95% significance level is recommended for this procedure. See (1)~~ 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.