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Standard Practice for Testing Homogeneity of Materials for Development of Reference Materials[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

1.1 This 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.

1.2 The 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.

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

1.4 This 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.

NOTE 1—**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 *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:*

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[2]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[3]

E 178 Practice for Dealing with Outlying Observations[3]

E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology E 135, and Practices E 177 and E 178.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *drift*—a gradual systematic or sinusoidal change in instrument readings with time.

3.2.2 *homogeneity—as defined in this practice*, is statistically acceptable differences among means of specimens in the test.

4. Summary of Practice

4.1 This procedure, which is based on statistical methods (**1-6**),[5] 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 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.

4.2 This 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.

[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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[2] *Annual Book of ASTM Standards*, Vol 03.05.

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

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

[5] The boldface numerals in parentheses refer to the list of references at the end of this practice.

TABLE 1 Data for Homogeneity Testing

Run No.	Specimen Number							Total
	1	2	3	4	5	...	...t^A	
1								B_1 =
2								B_2 =
3								B_3 =
4								B_4 =
5...								$B_{5...}$ =
...b^B								B_n =
Total	T_1 =	T_2 =	T_3 =	T_4 =	T_5 =	...	T_n =	$G = (\Sigma B_1 ... B_n)$
Mean	t'_1 =	t'_2 =	t'_3 =	t'_4 =	t'_5 =	...	t'_n =	

[A] t = number of specimens.
[B] b = number of runs.

4.3 This procedure requires that there be an absence of outliers in the data (see Practice E 178).

NOTE 2—**Caution:** 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.

5. Significance and Use

5.1 The 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.

5.2 This 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.

6. Selection of Test Specimens from a Large Batch

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

6.2 If 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.

6.3 Label all specimens consecutively (that is, 01, 02, 03,···). 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.

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

7. X-Ray Emission Spectroscopy Test Procedure

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

7.2 Select a counting time that is long enough to minimize the random error due to counting. Also, avoid counting rates greater than 70 000 c/s to minimize dead-time corrections in the detection system.

7.3 Measure 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.

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

7.5 Examine the data and discard any values which have been determined to be outliers according to Practice E 178. In Table 1, enter either the raw or normalized values for each element, or values corrected for drift.

7.6 If 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

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

8.2 Use 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.

8.3 Measure 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.

8.4 If 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.

8.5 Examine the data and discard any values that have been determined to be outliers according to Practice E 178. In Table 1, enter either the raw or normalized values for each element or values corrected for drift.

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

9. Calculations to Determine Homogeneity

9.1 Compute 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.

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

NOTE 4—A 95 % significance level is recommended for this procedure. See **(1)** for more extensive tables containing values at other significance levels.

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

$$\nu = (b - 1) \times (t - 1) \tag{1}$$

TABLE 2 Short Table of Random Numbers[A]

NOTE 1—**Caution:** See Note 3Note 3.

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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9.4 Compute S_t = sum of squares due to specimens:

$$S_t = [(T_1{}^2 + T_2{}^2 + \cdots T_t^2)/b] - (G^2/tb) \quad (2)$$

9.5 Compute S_b = sum of squares due to runs:

$$S_b = [(B_1{}^2 + B_2{}^2 + \cdots B_b^2)/t] - (G^2/tb) \quad (3)$$

9.6 Compute $\bar{S}$ = sum of the squares of all the measurements in the tables and subtract G^2/tb:

$$\bar{S} = (\sum_{i=1}^{t})(\sum_{j=1}^{b}) Y_{ij}{}^2 - (G^2/tb) \quad (4)$$

where:

Y_{ij} = individual values in the table.

9.7 Compute:

$$s = \sqrt{(\bar{S} - S_b - S_t)/(b-1)(t-1)} \quad (5)$$

9.8 Compute:

$$w = qs/\sqrt{b} \quad (6)$$

9.9 If the absolute difference between any two mean values (that is, $t'_1 \cdots t'_n$) exceeds w, then there is strong evidence, at the

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

ν ↓ / t→	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

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.

10. Test for Instrumental Drift

10.1 This test for drift is made on repeat analyses of the control reference material (C) measured along with the specimens (see Practice E 876). The control reference material is measured at the beginning of each test set and repeated after every three, five, or ten specimens have been run.

10.1.1 Select the control reference material frequency (such as, three, five, or ten) and maintain this measurement sequence throughout the entire test.

10.1.2 Arrange the measurements on the control reference material in the exact sequence in which they were made. For example: $C_1, C_2, C_3, \cdots C_n$.

10.1.3 Obtain the differences (Δ) between immediate successive measurements as follows:

$$\Delta_1 = C_1 - C_2; \Delta_2 = C_2 - C_3, \cdots \quad (7)$$

10.1.4 Calculate an estimate of variance S_1^2 as follows:

$$S_1^2 = \Sigma\Delta^2/(n - 1) \quad (8)$$

where:

Δ = difference between successive measurements, and
n = number of times the control reference material was run.

10.1.5 Calculate a second estimate of variance S_2^2 as follows:

$$S_2^2 = \Sigma d^2/(n - 1) \quad (9)$$

where:

d = difference of each measurement on the control reference material from the overall average of the measurements on the control.

10.1.6 Calculate the ratio:

$$S_1^2/S_2^2 (\mathbf{4\text{-}6}) \quad (10)$$

If the ratio S_1^2/S_2^2 is *larger* than the values listed in Table 4, for example, for the number of times the control reference material was measured, there is not sufficient evidence at the 95 % confidence level to indicate that drift has occurred. If no drift has occurred, the values obtained on the specimens should be tabulated in Table 1 in the order in which they were made,

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

Number of Measurements on Control Reference Material, n	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 (**4 and 5**). However, the values in the latter references are half the values shown in this table because of a slightly different method of dermination.