Designation: E 1060 – 85 (Reapproved 1995)[ε1]

Standard Practice for
Interlaboratory Testing of Spectrochemical Methods of Analysis[1]

This standard is issued under the fixed designation E 1060; 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.

[ε1] NOTE—Section 11 was added editorially in March 1995.

1. Scope

1.1 This practice describes techniques for planning and conducting an interlaboratory study of a spectrochemical method of analysis. It provides instructions for analyzing and interpreting the results, and for writing precision and accuracy statements.

1.2 The statistical definitions and procedures presented in this practice are limited, and are not intended to be exact or rigorous. If statistical procedures beyond the scope of this practice are required, consult Practices E 177, E 180, E 305, E 691, E 876, or other practices published by ASTM Committee E-11 on Statistical Methods; and *STP 335*.[2]

1.3 *This standard does not purport to address all of the safety problems, 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[3]
E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals[3]
E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[4]
E 180 Practice for Determining Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[5]
E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves[3]
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[4]
E 826 Practice for Testing Homogeneity of Materials for the Development of Reference Materials[6]

E 876 Practice for Use of Statistics in the Evaluation of Spectrochemical Data[6]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology E 135 and Practice E 876.

3.2 *Descriptions of Terms Specific to This Standard:*

3.2.1 *repeatability*—the precision obtained for analyses performed within the same laboratory on different days.

NOTE 1—In the event a question arises about the uniformity of variances across laboratories, refer to Practice E 691.

3.2.2 *reproducibility*—the precision obtained for analyses performed in different laboratories.

NOTE 2—In the event a question arises about the uniformity of variances across laboratories, refer to Practice E 691.

3.2.3 *systematic error*—a displacement of all or most of the analytical results from the "true" or reference value that is caused by some constant or proportional error (bias) in the analytical method or procedure.

4. Significance and Use

4.1 This practice is useful for designing an interlaboratory test, for evaluating the precision and accuracy of spectrochemical methods of analysis, and for writing precision and accuracy statements.

5. Procedure for Cooperative Testing

5.1 The procedures described in this section shall be performed or administered by a task group with a chairman:

5.1.1 Select cooperating laboratories. Five or more laboratories are recommended to demonstrate the reliability of the method. (See Note 3.) Fewer laboratories may be used; however, no fewer than three laboratories shall participate in any evaluation. Also, the product of the number of laboratories, test specimens, and determinations per element shall equal 45 or greater. For supporting information, refer to *STP 335*.

NOTE 3—It is the opinion of some that with data from fewer than eight laboratories, reproducibility calculations are not reliable, consequently statements on reproducibility should not be included in the standard method.

5.1.2 Contact each of the laboratories selected and obtain a commitment to cooperate in the test program.

5.1.3 Send a copy of the method to be evaluated to each of the cooperating laboratories. This is to ensure that each laboratory understands the procedure, and has the necessary

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[1] This practice is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry of Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.22 on Statistics and Quality Control.
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[2] *Manual for Conducting an Interlaboratory Study of a Test Method, ASTM STP 335*, ASTM, 1963. Available from University Microfilms International, 300 North Zeeb Road, Ann Arbor, MI 48106.
[3] *Annual Book of ASTM Standards*, Vol 03.05.
[4] *Annual Book of ASTM Standards*, Vol 14.02.
[5] *Annual Book of ASTM Standards*, Vol 15.05.
[6] *Annual Book of ASTM Standards*, Vol 03.06.

equipment and qualified personnel. A laboratory should practice an unfamiliar procedure prior to performing the interlaboratory test. *All cooperating laboratories must agree upon the exact manner in which the test method is to be implemented. Resolve any question concerning the method or how it is to be implemented prior to starting the test.*

5.1.3.1 "Practice" test specimens will be furnished by the task group when requested.

5.1.4 Establish a timetable with firm deadlines (see Fig. X1.1). The task group is responsible for timely data evaluation and publication of results.

5.1.5 Select test specimens to adequately cover the analytical range of each element as specified in the scope of the method being tested. The test specimens shall span the low, medium, and high portions of the specified range. However, for narrow ranges, test specimens at two levels of concentration may be adequate. Specimens for testing shall be certified reference materials if possible. If it is necessary to use uncertified reference materials for testing, the composition shall be established using the following guidelines:

5.1.5.1 Confirm the homogeneity of the test specimens, as heterogeneous specimens will affect the precision estimates of the method. If a homogeneity test is required, refer to Practice E 826.

5.1.5.2 Determine each element using more than one analytical technique when possible, excluding the technique being tested.

5.1.6 Select reference materials to be used for calibration of the instrument. Where possible, use reference materials and test specimens that have similar compositions, metallurgical structure and other features.

5.1.7 Provide the same reference materials and test specimens to all participants:

5.1.7.1 If solutions are to be analyzed, send a separate set of reference and specimen solutions to each cooperating laboratory.

5.1.7.2 If powders or chips are to be analyzed, send separate portions of the reference materials and specimens to each cooperating laboratory.

5.1.7.3 If solid specimens (such as disks) are employed, send the same set of reference materials and test specimens to each laboratory. However, when certified reference materials of known and acceptable homogeneity are used, send separate pieces to each cooperator. This will expedite testing. When all laboratories must test the same reference materials and specimens, send them to Laboratory A and request that they be returned to the task group. The task group will then send the same reference materials and specimens to Laboratory B for analysis. This round-robin procedure will be continued until all cooperators have completed the test.

5.1.8 Send the items listed below to each of the cooperating laboratories, preferably in the same package or at the same time (see Fig. X1.2):

5.1.8.1 Reference materials to be used.

5.1.8.2 Test specimens to be analyzed.

5.1.8.3 Instructions specifying the method or procedure to be tested.

5.1.8.4 Copy of the method or procedure to be used.

5.1.8.5 Forms to be completed by cooperators (see Figs. X2.1, X2.2, and X2.3).

5.1.8.6 Instructions that specify the operating conditions

that are to be reported by the cooperating laboratory (see Fig. X2.1).

5.1.8.7 Instructions from the task group specifying the exact order for analyzing reference materials and specimens to randomize data, the element(s) to be determined in each specimen, and the number of determinations for each element.

5.1.8.8 Instructions specifying the number of replications for reference materials and specimens. Generally, the analytical curve for each element shall be established with four replications (runs) on each reference material. Use the "$4n$" rule given in Practice E 305 for the cooperative test, unless the task group specifies otherwise. Define the number of replications (runs) that will be averaged to produce an analysis (average result). The task group shall specify how individual laboratories are to treat outliers that may occur during the replications.

5.1.8.9 Instructions for documenting any specific departure(s) from the method being used (see Fig. X2.2).

5.1.8.10 Instructions specifying the number of significant figures that are to be reported for each element. For purposes of statistical evaluation, the number of significant figures should be one more than normally is required.

5.1.8.11 Instructions for reporting the final results (see Fig. X2.3). To simplify data evaluation, report all values for an element on the same form. Use a separate form for each element.

5.1.9 Whenever possible, specify allowable (acceptable) analytical tolerance for the method in advance of testing. These tolerances shall be determined by the task group and should be based on:

5.1.9.1 The analytical performance required to meet the need.

5.1.9.2 Previous experience with similar methods of analysis, if available.

5.1.9.3 Knowledge of typical bias between laboratories for the material analyzed and analytical technique used.

NOTE 4—The analytical tolerance of a method may be very broad or narrow depending on its intended use. It is the responsibility of the task group to determine the acceptable tolerance, recognizing that in some cases it may not be possible to establish a tolerance prior to evaluation. Similarly, the criteria for laboratory bias should be defined in advance of the test, for example, by establishing a difference allowed between the extreme laboratory and the next closest laboratory.

5.1.10 Maintain records identifying the cooperating laboratories and analysts. Assign a code to each laboratory (see Fig. X1.1).

5.1.11 Maintain data from all laboratories for each element determined on a copy of the evaluation form shown in Fig. X1.3.

5.1.12 Evaluate the cooperative test data as described in Section 6 and recommend the disposition of the method including, but not limited to, the following: (*1*) acceptance, (*2*) rejection, (*3*) additional testing, or (*4*) acceptance of the method, but with reduced analytical tolerances as defined in 5.1.9. Submit *all test data*, along with a summary of the test data and the recommendation to the subcommittee chairman, who, in turn, submits the material to the Chairman of ASTM Committee E-2.

5.1.13 Following the guidelines given in Sections 7 and 8, write precision and accuracy statements for inclusion in the

draft of the method to be submitted for committee ballot.

5.1.14 Tabulate performance data and include them in the method.

5.1.15 Revise the method to conform to the conditions explicitly followed in the test.

6. Evaluation of Cooperative Test Data

6.1 Examine the test results for possible outliers, as described in Practice E 876. Analyses defined as outliers at the 95 % probability limit shall be discarded and, if possible, replaced with additional test data. If such data cannot be replaced, replace the missing data point with the average value from the other laboratories.

6.2 Examine data from each laboratory for systematic error (bias) using the test described in Practice E 876. Results from a laboratory showing systematic error greater than that specified shall be discarded (see 5.1.9) and, if feasible, replaced with additional test data. If such data cannot be replaced, calculate the performance without that laboratory as shown in Table X3.2.

6.3 Evaluate the interlaboratory test data by *analysis of variance* as described in Practice E 173. A simplified, step-by-step procedure for *analysis of variance*, based on Practice E 173, is given below:

6.3.1 *Tabulation:*

6.3.1.1 Record the results for each element on separate copies of the evaluation form given in Fig. X1.3, in accordance with 5.1.11 (see Appendix X3 for an example of a completed form with the calculations included).

6.3.1.2 Sum the results from each laboratory, ΣX_j, and enter the sum in the column headed by ΣX_j in Fig. X1.3.

6.3.1.3 Sum all results from all laboratories (sum ΣX_j column) and enter at $\Sigma(\Sigma X_{ij})$ on Fig. X1.3.

6.3.1.4 Calculate the average value, $\bar{X}$, and enter on Fig. X1.3. Calculate as follows:

$$\bar{X} = \Sigma(\Sigma X_{ij})/np \qquad (1)$$

where:

n = number of results from each laboratory (replicates) for the element measured, and

p = number of laboratories.

6.3.1.5 Square the sum of the results from each laboratory, $(\Sigma X_j)^2$, and enter that value in the column headed $(\Sigma X_j)^2$ on Fig. X1.3.

6.3.1.6 Sum all the squares of the sum of the results from each laboratory, $\Sigma(\Sigma X_j)^2$, and enter at $\Sigma(\Sigma X_j)^2$ on Fig. X1.3.

6.3.2 *Analysis of Variance Calculations*—The equations listed below are given in the lower half of Fig. X1.3. Record all calculations on Fig. X1.3 (see Table X3.2).

6.3.2.1 *Calculation 1*—Square each result and sum all the squared values, ΣX^2.

6.3.2.2 *Calculation 2*—Calculate the correction term, CT, as follows:

$$CT = [\Sigma(\Sigma X_{ij})]^2/np \qquad (2)$$

where $\Sigma(\Sigma X_{ij})$ = the value from 6.3.1.3.

6.3.2.3 *Calculation 3*—Calculate the "sum of the squares for total," SST, as follows:

$$SST = \Sigma X^2 - CT \qquad (3)$$

where ΣX^2 = the value obtained from 6.3.2.1.

6.3.2.4 *Calculation 4*—Calculate the "sum of the squares

TABLE 1 $F_{0.05}$ Distribution ($P = 0.95$)[A]

df_2/df_1[B]	3	4	5	6	7
6	4.76	4.53	4.39	4.28	4.21
8	4.07	3.84	3.69	3.58	3.50
9	3.86	3.63	3.48	3.37	3.29
10	3.71	3.48	3.33	3.22	3.14
12	3.49	3.26	3.11	3.00	2.92
14	3.34	3.11	2.96	2.85	2.77
15	3.29	3.06	2.90	2.79	2.70
16	3.24	3.01	2.85	2.74	2.66
18	3.16	2.93	2.77	2.66	2.58
20	3.10	2.87	2.71	2.60	2.52
21	3.07	2.84	2.68	2.57	2.49
24	3.01	2.78	2.62	2.51	2.43
25	2.99	2.76	2.60	2.49	2.41
28	2.95	2.71	2.56	2.44	2.36
30	2.92	2.69	2.53	2.42	2.34
35	2.87	2.64	2.49	2.37	2.29

[A] A complete tabulation of F values is given in most statistical handbooks.

[B] df_1 is associated with laboratories ($p - 1$), and df_2 is associated with values ($n - 1$). In Tables of F values, the symbols v_1 and v_2 are sometimes used in place of df_1 and df_2.

between laboratories," SSL, as follows:

$$SSL = [\Sigma(\Sigma X_j)^2]/n - CT \qquad (4)$$

where $\Sigma(\Sigma X_j)^2$ = the value obtained from 6.3.1.6.

6.3.2.5 *Calculation 5*—Calculate the "sum of the squares within laboratories," SSW, as follows:

$$SSW = SST - SSL \qquad (5)$$

6.3.2.6 *Calculation 6*—Calculate the "mean square between laboratories," MSL, as follows:

$$MSL = SSL/(p - 1) \qquad (6)$$

6.3.2.7 *Calculation 7*—Calculate the "mean square within laboratories," MSW, as follows:

$$MSW = SSW/p(n - 1) \qquad (7)$$

NOTE 5—MSW is the variance within laboratories, which is usually shown as s_w^2.

6.3.2.8 *Calculation 8*—Calculate the F ratio of the means, as follows:

$$F = MSL/MSW \qquad (8)$$

Compare the calculated F value with the appropriate $F_{0.05}$ value from Table 1. In using Table 1, v_1 = the degrees of freedom of MSL and df = the degrees of freedom of MSW. If the calculated value of F is less than the $F_{0.05}$ value taken from Table 1, there is no statistical evidence, at 95 % probability, of significant differences between laboratories. Consequently, data from all laboratories should be evaluated. If the calculated F value is greater than the $F_{0.05}$ value taken from Table 1, there is strong evidence, at 95 % probability, that the results from one or more laboratories are statistically different from the others. If one laboratory is clearly the source of the statistically different values, discard the results from that laboratory and reevaluate the data from the remaining laboratories. If, however, the results from more than one laboratory are shown to be statistically different, two alternatives should be considered, as follows: (*1*) Seek help to provide a more detailed statistical evaluation of the data to decide which laboratories should be discarded and if the remaining data are adequate to support the analytical method. (*2*) Repeat the interlaboratory test under closer control.

TABLE 2 Factors (F_d) for Calculating Range of Two Results (At 95 % Probability Limit)[A]

Degrees of Freedom (df)	F_d	Degrees of Freedom (df)	F_d
1	17.97	16	3.00
2	6.09	17	2.98
3	4.50	18	2.97
4	3.93	19	2.96
5	3.64	20	2.95
6	3.46	22	2.93
7	3.34	24	2.92
8	3.26	26	2.91
9	3.20	28	2.90
10	3.15	30	2.89
11	3.11	40	2.86
12	3.08	50	2.84
13	3.05	60	2.83
14	3.03	120	2.80
15	3.01	∞	2.77

[A] Data taken from Practice E 180 and consists of values from standard student's t-table that have been multiplied by $\sqrt{2}$ to reflect that two results are under consideration.

6.3.2.9 *Calculation 9*—Calculate the estimate of standard deviation of any single random analysis within laboratories, s_w, as follows:

$$s_w = \sqrt{MSW} \qquad (9)$$

6.3.2.10 *Calculation 10*—Calculate the estimate of variance between laboratories, s_L^2, as follows:

$$s_L^2 = \frac{1}{n}(MSL - MSW) \qquad (10)$$

6.3.2.11 *Calculation 11*—Calculate s_{SR}, which is needed later to calculate R_2, as follows:

$$s_{SR} = \sqrt{s_L^2 + (s_w^2/m)} \qquad (11)$$

where m = the number of analyses that are averaged to obtain the reported value.

NOTE 6—In most cases, each reported value is based on a single analysis. When that occurs, $m = 1$.

6.3.2.12 *Calculation 12*—Calculate an approximation of the acceptable limits or range, at 95 % probability limits, of a pair of analyses from the same laboratory, R_1, as follows:

$$R_1 = F_d(s_w/\sqrt{m}) \qquad (12)$$

where F_d = the appropriate factor from Table 2 [degrees of freedom for within-laboratory cases = $p(n-1)$], and s_w is from 6.3.2.9.

6.3.2.13 *Calculation 13*—Calculate an approximation of the acceptance limits or range, at 95 % probability limits, of a pair of analyses from different laboratories, R_2, as follows:

$$R_2 = F_d(s_{SR}) \qquad (13)$$

where:

F_d = the appropriate factor from Table 2 (degrees of freedom for between-laboratory cases = $p - 1$), and
s_{SR} is from 6.3.2.11.

NOTE 7—Practice E 173 uses $2\sqrt{2}$ in place of F_d to calculate R_1 and R_2. Use of $2\sqrt{2}$ provides an acceptable approximation of the range of duplicates provided the calculations of s_w and s_{SR} were based on at least 20 df. To obtain an even rougher estimate of acceptable limits (95 % probability limits), simply multiply the appropriate standard deviation by three, then $R = 3s$.

6.3.2.14 Summarize the performance data as shown in Table X3.2.

6.4 *Accuracy*—Calculate an estimate of overall accuracy, s_a, for a single analysis from any laboratory at the 95 % probability limit as follows:

$$s_a = 2\sqrt{\Sigma(d_t)^2/(q-1)} \qquad (14)$$

where:

d_t = difference of individual test results from the assumed "true" value of the sample tested, and
q = total number of analyses from all laboratories.

NOTE 8—This equation provides a useful measure of accuracy. If a more precise measure of accuracy is essential, use a "t" value for $q - 1$ degrees of freedom in place of the constant 2. The equation then becomes $s_a = t\sqrt{\Sigma d_t^2/(q-1)}$. For evaluation of most spectrochemical data, use of 2 instead of a "t" value is adequate except when the total number of analyses is fewer than 15.

7. Precision Statements

7.1 Use values obtained in 6.3.2.9 (s_w), 6.3.2.11 (s_{SR}), 6.3.2.12 (R_1), and 6.3.2.13 (R_2) to prepare statements of repeatability (within-laboratory precision), and reproducibility (between-laboratory precision). State the deviation of results, degrees of freedom and maximum difference expected at the 95 % probability limit between two results on the same sample, and where appropriate, include information regarding (*1*) average concentration, (*2*) number of laboratories, (*3*) number of analysts, (*4*) period of test, and (*5*) degrees of freedom. Refer to Practice E 173 for additional information regarding the terms precision and accuracy. Suggested formats for precision statements to be included in methods for committee ballot are as follows:

7.1.1 *Repeatability*—At an average concentration of __ %, the estimated standard deviation of results obtained by the same analyst on different days is calculated to be __ % absolute at __ df. Two values from the same laboratory shall be considered suspect (at the 95 % probability limit) if they differ by more than __ % absolute.

7.1.2 *Reproducibility*—At an average concentration of __ %, the estimated standard deviation of results obtained by analysts in different laboratories is calculated to be __ % absolute at __ df. Two values from different laboratories shall be considered suspect (at the 95 % probability limit) if they differ by more than __ % absolute. (See Note 3.)

7.1.3 If more than one specimen is tested for an element, the analytical data may be pooled statistically to provide a consensus statement of performance for that element. However, if a number of elements are determined in each test specimen, or if a broad concentration range is covered for each element, it may be simpler to tabulate the analytical performance data in a table rather than to make a performance statement for each element and concentration range. When applicable, the performance statements shall be shortened appropriately and reference shall be made to the tables summarizing the data. Examples of such tables, summarizing both precision and accuracy data, are given in Tables X3.3 and X3.4.

8. Accuracy Statements

8.1 Provide the following information in accuracy statements:

8.1.1 The expected agreement (accuracy) between the individual test results and the "true" value as determined in 6.4.

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