Designation: E 180 – 03

Standard Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals[1]

This standard is issued under the fixed designation E 180; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice establishes uniform standards for expressing the precision and bias of test methods for industrial and specialty chemicals. It includes an abridged procedure for developing this information, based on the simplest elements of statistical analysis. There is no intent to restrict qualified groups in their use of other techniques.

1.2 *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.*

1.3 In this practice, the vocabulary and guidelines for calculation and interpretation of statistical data according to the ISO are followed as closely as possible. Particular reference is made to ISO 5725, Parts 1 to 6.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D 1013 Test Method for Total Nitrogen in Resins and Plastics

D 1727 Test Method for Urea Content of Nitrogen Resins

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specification

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

E 178 Practice for Dealing with Outlying Observations

E 456 Terminology Relating to Quality and Statistics

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E 1169 Guide for Conducting Ruggedness Tests

2.2 *ISO Document:*

ISO 5725 Accuracy (trueness and precision) of measurements and results[3]

3. Significance and Use

3.1 All test methods require statements of precision and bias. The information for these statements is generated by an interlaboratory study (ILS). This practice provides a specific design and analysis for the study, and specific formats for the precision and bias statements. It is offered primarily for the guidance of task groups having limited statistical experience.

3.2 It is recognized that the use of this simplified procedure will sacrifice considerable information that could be developed through other designs or methods of analyzing the data. For example, this practice does not afford any estimate of error to be expected between analysts within a single laboratory. Statements of precision are restricted to those variables specifically mentioned. Task groups capable of handling the more advanced procedures are referred to the literature **(1, 2, 3, 5, 13)**[4] and specifically to Practice E 691, the current Committee E11 practice for interlaboratory studies. The latter includes graphical display and interpretation of ILS data.

3.3 The various parts appear in the following order:

Part A—Glossary.
Part B—Preliminary Studies.
Part C—Planning the Interlaboratory Study.
Part D—Testing for Outlying Observations.
Part E—Statistical Analysis of Collaborative Data.
Part F—Format of Precision Statements.
Part G—Bias (Systematic Error).
Part H—Presentation of Data.

[1] This practice is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and is the direct responsibility of Subcommittee E15.01 on General Standards.

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

[3] Available from International Organization for Standardization (ISO), 1 Rue de Varembé, Case postale 56, CH-1211 Geneva 20, Switzerland.

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

4. Keywords

4.1 bias; industrial chemicals; interlaboratory study; precision; specialty chemicals

PART A—GLOSSARY

5. Scope

5.1 The following statistical terms are defined in the sense in which they will be used in presenting precision and bias information. These definitions have been simplified and are not necessarily universally acceptable nor as defined in Terminology E 456 and Practice E 177. For definitions and explanations of other statistical terms used in this practice, refer to Terminology E 456 and Practice E 177.

6. Terminology

6.1 *Definitions and Descriptions of Terms:*

6.1.1 *accuracy*—the agreement between an experimentally determined value and the accepted reference value. In chemical work, this term is frequently used to express freedom from bias, but in other fields it assumes a broader meaning as a joint index of precision and bias (see Practice E 177 and **(4)**). To avoid confusion, the term "bias" will be used in appraising the systematic error of test methods for industrial chemicals.

6.1.2 *bias*—a constant or systematic error as opposed to a random error. It manifests itself as a persistent positive or negative deviation of the method average from the accepted reference value.

6.1.3 *coefficient of variation*—a measure of relative precision calculated as the standard deviation of a series of values divided by their average. It is often multiplied by 100 and expressed as a percentage.

6.1.4 *duplicates*—two independent determinations performed by one analyst at essentially the same time.

6.1.5 *error*—in a statistical sense, any deviation of an observed value from the true, but generally unknown value. When expressed as a fraction or percentage of the value measured, it is called a relative error. All statements of precision or bias should indicate clearly whether they are expressed in absolute or relative sense.

6.1.6 *laboratory precision (within-laboratory, between-days variability)*—the precision of a method expressed as the agreement attainable between independent determinations (each the average of duplicates) performed by one analyst using the same apparatus and techniques on each of two days. (This term is further defined and limited in 10.1.6, 25.1, and 25.2.9.2) **(12)**.

6.1.7 *precision*—the degree of agreement of repeated measurements of the same property. Precision statements in ASTM methods for industrial and specialty chemicals will be derived from the estimated standard deviation or coefficient of variation of a series of measurements and will be expressed in terms of the repeatability; the within-laboratory, between days variability; and the reproducibility of a method (see 6.1.14, 6.1.3, 6.1.10, 6.1.16, 6.1.12).

6.1.8 *random error*—the chance variation encountered in all experimental work despite the closest possible control of variables. It is characterized by the random occurrence of both positive and negative deviations from the mean value for the method, the algebraic average of which will approach zero in a long series of measurements.

6.1.9 *range*—the absolute value of the algebraic difference between the highest and the lowest values in a set of data.

6.1.10 *repeatability*—the precision of a method expressed as the agreement attainable between two independent determinations performed at essentially the same time (duplicates) by one analyst using the same apparatus and techniques. (see also 6.1.6.)

6.1.11 *replicates*—two or more repetitions of a test determination.

6.1.12 *reproducibility*—the precision of a method expressed as the agreement attainable between determinations performed in different laboratories **(12)**.

6.1.13 *result*—a value obtained by carrying out the test method. The value can be a single determination, an average of duplicates, or other specified grouping of replicates.

6.1.14 *significance level*—the decimal probability that a result will exceed the critical value. (see 21.3 and 21.4.)

6.1.15 *standard deviation*—a measure of the dispersion of a series of results around their average, expressed as the positive square root of the quantity obtained by summing the squares of the deviations from the average of the results and dividing by the number of observations minus one. It is also the square root of the variance and can be calculated as follows:

$$s = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n - 1}} \quad (1)$$

where:

s = estimated standard deviation of the series of results,
X_i = each individual value,
$\bar{X}$ = average (arithmetic mean) of all values, and
n = number of values.

The following forms of this equation are more convenient for computation, especially when using a calculator:

$$s = \sqrt{\frac{\Sigma X^2 - (\Sigma X)^2/n}{n - 1}} \quad (2)$$

or

$$s = \sqrt{\frac{n\Sigma X^2 - (\Sigma X)^2}{n(n - 1)}} \quad (3)$$

where:

s = estimated standard deviation,
ΣX^2 = sum of the squares of all of the individual values,
$(\Sigma X)^2$ = square of the total of the individual values, and
n = number of values.

NOTE 1—Care must be taken in using either of these equations that a sufficient number of decimal places is carried in the sum of the values and in the sum of their squares so that serious rounding errors do not occur. For best results, all rounding should be postponed until after a value has been obtained for *s*.

In this practice, the standard deviation is obtained from the difference between duplicate determinations and from an analysis of variance of an interlaboratory test program (see Part E).

6.1.16 *variance*—a measure of the dispersion of a series of results around their average. It is the sum of the squares of the

individual deviations from the average of the results, divided by the number of results minus one.

6.1.17 *95 % limit (difference between two results)*—the maximum absolute difference expected for approximately 95 % of all pairs of results from laboratories similar to those in the interlaboratory study.

PART B—PRELIMINARY STUDIES

7. Scope

7.1 This part covers the preliminary work that should be carried out in a few laboratories before undertaking a full interlaboratory evaluation of a method.

8. Discussion

8.1 When a task group is asked to provide a specific test procedure, there may be available one or more methods from the literature or from laboratories already performing such analyses. In such cases, these methods have usually been the subject of considerable research and any additional study of variables, at this stage, would be wasteful of available task group time. It is recommended that such methods be rewritten in ASTM format, with full descriptions of the equipment and procedure, and be evaluated in a pilot run by a few laboratories on selected materials. Three laboratories and at least three such materials, using one or two analysts performing duplicate determinations on each of two days, by each method, constitutes a practical plan which can be analyzed by the procedures described in Part E—Statistical Analysis of Collaborative Data. Such a pilot study will confirm the adequacy of the methods and supply qualitative indications of relative precision and bias.

8.2 When the method to be evaluated is new, or represents an extensive modification of an available method, it is recommended that a study on variables be carried out by at least one laboratory to establish the parameters and conditions to be used in the description of the method. This should be followed by a three-laboratory pilot study before undertaking a full interlaboratory evaluation.

8.3 Detailed procedures for executing such preliminary studies are not described in this practice but are available in the general statistical literature.[5] Practice E 691 and Guide E 1169 also provide information on this subject.

PART C—PLANNING THE INTERLABORATORY STUDY

9. Scope

9.1 This part covers some commonsense recommendations for the planning of interlaboratory studies.

10. Variables

10.1 The major variables to be considered are the following: methods, materials or levels, laboratories, apparatus, analysts, days, and runs. These are discussed as follows:

10.1.1 *Methods*—The preliminary studies of Part B should lead to agreement on a single method, which can then be evaluated in a full interlaboratory study. If it is necessary to evaluate two or more methods, the complete program must be carried out on each such method. In either case, it will be assumed that the method variables have been explored and that a well-standardized, fully detailed procedure has been prepared. Nothing short of this will justify the time and expense required for an extensive precision study.

10.1.2 *Materials or Levels*—The number of samples distributed should be held to the minimum needed to evaluate the method adequately. (Increasing the number of samples will not increase significantly the degrees of freedom (see 25.2.8) available for predicting the reproducibility of the method. This can be achieved only by increasing the number of laboratories.) Some interlaboratory studies can be limited to a single sample, as in the case of preparing a specific standard solution. Methods applicable to a single product of high purity can usually be evaluated with one or two samples. When different concentrations of a constituent or values of a physical property are involved, the samples should represent the approximate lower, middle, and top levels of the expected range. If these vary over a wide range, the number of levels should be increased and spaced to cover the range. If technical grade products are used in a precision study, the bias of the method may be undeterminable unless the accepted reference value and its limits of error are known from other sources. For this reason, it is well to include one or more samples of known purity in the interlaboratory study.

10.1.3 *Laboratories*—To obtain a reliable precision estimate, it is recommended that the interlaboratory study include approximately ten qualified laboratories.[6] When this number of independent laboratories cannot be recruited, advantage can be taken of a liberalized definition of collaborating laboratories, quoted as follows from the *ASTM Manual for Conducting an Interlaboratory Study of a Test Method* (*STP 335*), p. 9 **(5)**:

Here the term “collaborating laboratory” has a more specific meaning than in common usage. For example, a testing process often consists of an integrated sequence of operations using apparatus, reagents, and measuring instruments; and several more or less independent installations may be set up in the same area or “laboratory.” Each such participating installation should be considered as a collaborating laboratory so far as this procedure is concerned. Similarly, sets of test results obtained with different participants or under different conditions of calibration would in general constitute results from different collaborating laboratories even though they were obtained on the same sets of equipment.

This concept makes it possible to increase the available “laboratories” by using two analysts (but not more than two) in as many laboratories as needed to bring the total to the recommended minimum of ten. In such cases the two analysts must evaluate the method independently in the fullest sense of the word, interpreted as using different samples, different reagents, different apparatus where possible, and performing

[5] Task group chairmen are referred specifically to Youden, W. J. “Experimental Design and ASTM Committees,” *Materials Research & Standards*, MTRSA Vol 1, No. 11, November 1961, p. 862.

[6] Practice E 691 insists on a minimum of six laboratories, but would prefer more than ten.