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Standard Practice for Statistical Treatment of Thermoanalytical Data¹

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1. Scope

1.1 This practice details the statistical data treatment used in some thermal analysis methods.

1.2 The method describes the commonly encountered statistical tools of the mean, standard deviation, relative standard deviation, pooled standard deviation, pooled relative standard deviation and the best fit to a straight line, all calculations encountered in thermal analysis methods.

1.3 Some thermal analysis methods derive the analytical value from the slope or intercept of a best fit straight line assigned to three or more sets of data pairs. Such methods may require an estimation of the precision in the determined slope or intercept. The determination of this precision is not a common statistical tool. This practice details the process for obtaining such information about precision.

1.4 There are no ISO methods equivalent to this practice.

2. Referenced Documents

2.1 *ASTM Standards*:²

[E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods](#)

[E456 Terminology Relating to Quality and Statistics](#)

[E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method](#)

[E2161 Terminology Relating to Performance Validation in Thermal Analysis](#)

[F1469 Guide for Conducting a Repeatability and Reproducibility Study on Test Equipment for Nondestructive Testing](#)

3. Terminology

3.1 *Definitions*—The technical terms used in this practice are defined in Practice [E177](#) and Terminologies [E456](#) and

[E2161](#) including *precision, relative standard deviation, repeatability, reproducibility, slope, standard deviation, thermoanalytical, and variance.*

3.2 Symbols:³

m	= slope
b	= intercept
n	= number of data sets (that is, x_p, y_i)
x_i	= an individual independent variable observation
y_i	= an individual dependent variable observation
Σ	= mathematical operation which means “the sum of all” for the term(s) following the operator
$\bar{X}$	= mean value
s	= standard deviation
s_{pooled}	= pooled standard deviation
s_b	= standard deviation of the line intercept
s_m	= standard deviation of the slope of a line
s_y	= standard deviation of Y values
RSD	= relative standard deviation
δy_i	= variance in y parameter
r	= correlation coefficient
R	= gage reproducibility and repeatability (see Guide F1469) an estimation of the combined variation of repeatability and reproducibility ⁴
s_r	= within laboratory repeatability standard deviation (see Practice E691)
s_R	= between laboratory repeatability standard deviation (see Practice E691)

4. Summary of Practice

4.1 The result of a series of replicate measurements of a value are typically reported as the mean value plus some estimation of the precision in the mean value. The standard deviation is the most commonly encountered tool for estimating precision, but other tools, such as relative standard deviation or pooled standard deviation, also may be encountered in specific thermoanalytical test methods. This practice describes the mathematical process of achieving mean value, standard deviation, relative standard deviation and pooled standard deviation.

¹ This practice is under the jurisdiction of ASTM Committee [E37](#) on Thermal Measurements and is the direct responsibility of Subcommittee [E37.10](#) on Fundamental, Statistical and Mechanical Properties.

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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 Taylor, J.K., *Handbook for SRM Users, Publication 260-100*, National Institute of Standards and Technology, Gaithersburg, MD, 1993.

⁴ *Measurement System Analysis*, third edition, Automotive Industry Action Group, Southfield, MI, 2003, pp. 55, 177–184.

4.2 In some thermal analysis experiments, a linear or a straight line, response is assumed and desired values are obtained from the slope or intercept of the straight line through the experimental data. In any practical experiment, however, there will be some uncertainty in the data so that results are scattered about such a straight line. The least squares method is an objective tool for determining the “best fit” straight line drawn through a set of experimental results and for obtaining information concerning the precision of determined values.

4.2.1 For the purposes of this practice, it is assumed that the physical behavior, which the experimental results approximate, are linear with respect to the controlled value, and may be represented by the algebraic function:

$$y = mx + b \quad (1)$$

4.2.2 Experimental results are gathered in pairs, that is, for every corresponding x_i (controlled) value, there is a corresponding y_i (response) value.

4.2.3 The best fit approach assumes that all x_i values are exact and the y_i values (only) are subject to uncertainty.

NOTE 1—In experimental practice, both x and y values are subject to uncertainty. If the uncertainty in x_i and y_i are of the same relative order of magnitude, other more elaborate fitting methods should be considered. For many sets of data, however, the results obtained by use of the assumption of exact values for the x_i data constitute such a close approximation to those obtained by the more elaborate methods that the extra work and additional complexity of the latter is hardly justified.^{5,4}

4.2.4 The best fit approach seeks a straight line, which minimizes the uncertainty in the y_i value.

5. Significance and Use

5.1 The standard deviation, or one of its derivatives, such as relative standard deviation or pooled standard deviation, derived from this practice, provides an estimate of precision in a measured value. Such results are ordinarily expressed as the mean value $\pm$ the standard deviation, that is, $\bar{X} \pm s$.

5.2 If the measured values are, in the statistical sense, “normally” distributed about their mean, then the meaning of the standard deviation is that there is a 67 % chance, that is 2 in 3, that a given value will lie within the range of $\pm$ one standard deviation of the mean value. Similarly, there is a 95 % chance, that is 19 in 20, that a given value will lie within the range of $\pm$ two standard deviations of the mean. The two standard deviation range is sometimes used as a test for outlying measurements.

5.3 The calculation of precision in the slope and intercept of a line, derived from experimental data, commonly is required in the determination of kinetic parameters, vapor pressure or enthalpy of vaporization. This practice describes how to obtain these and other statistically derived values associated with measurements by thermal analysis.

6. Calculation

6.1 Commonly encountered statistical results in thermal analysis are obtained in the following manner.

NOTE 2—In the calculation of intermediate or final results, all available figures shall be retained with any rounding to take place only at the expression of the final results according to specific instructions or to be consistent with the precision and bias statement.

6.1.1 The mean value ($\bar{X}$) is given by:

$$\bar{X} = \frac{x_1 + x_2 + x_3 + \dots + x_i}{n} = \frac{\sum x_i}{n} \quad (2)$$

6.1.2 The standard deviation (s) is given by:

$$s = \left[\frac{\sum (x_i - \bar{X})^2}{(n - 1)} \right]^{1/2} \quad (3)$$

6.1.3 The Relative Standard Deviation (RSD) is given by:

$$RSD = (s \cdot 100 \%) / \bar{X} \quad (4)$$

6.1.4 The Pooled Standard Deviation (s_p) is given by:

$$s_p = \left[\frac{(\{n_1 - 1\} \cdot s_1^2) + (\{n_2 - 1\} \cdot s_2^2) + \dots + \sum (\{n_i - 1\} \cdot s_i^2)}{(n_1 - 1) + (n_2 - 1) + \dots + (n_i - 1)} \right]^{1/2} \quad (5)$$

$$= \left[\frac{\sum (\{n_i - 1\} \cdot s_i^2)}{\sum (n_i - 1)} \right]^{1/2} \quad (6)$$

NOTE 3—For the calculation of pooled relative standard deviation, the values of s_i are replaced by RSD_i .

6.1.5 The Gage Repeatability and Reproducibility (R) is given by:

$$R = [s_r^2 + s_r^2]^{1/2} \quad (7)$$

NOTE 4—For the calculation of relative Gage Repeatability and reproducibility, the values of s_r and s_R are replaced with RSD_r and RSD_R .

6.2 *Best Fit to a Straight Line:*

6.2.1 The best fit slope (m) is given by:

$$m = \frac{n \sum (x_i y_i) - (\sum x_i) (\sum y_i)}{n \sum x_i^2 - (\sum x_i)^2} \quad (8)$$

6.2.2 The best fit intercept (b) is given by:

$$b = \frac{(\sum x_i^2) (\sum y_i) - (\sum x_i) (\sum x_i y_i)}{n \sum x_i^2 - (\sum x_i)^2} \quad (9)$$

6.2.3 The individual dependent parameter variance (δy_i) of the dependent variable (y_i) is given by:

$$\delta y_i = y_i - (mx_i + b) \quad (10)$$

6.2.4 The standard deviation s_y of the set of y values is given by:

$$s_y = \left[\frac{\sum (\delta y_i)^2}{n - 2} \right]^{1/2} \quad (11)$$

6.2.5 The standard deviation (s_m) of the slope is given by:

$$s_m = s_y \left[\frac{n}{n \sum x_i^2 - (\sum x_i)^2} \right]^{1/2} \quad (12)$$

6.2.6 The standard deviation (s_b) of the intercept (b) is given by:

$$s_b = s_y \left[\frac{\sum x_i^2}{n \sum x_i^2 - (\sum x_i)^2} \right]^{1/2} \quad (13)$$

6.2.7 The denominators in Eq 8, Eq 9, Eq 12, and Eq 13 are the same. It is convenient to obtain the denominator (D) as a separate function for use in manual calculation of each of these equations.

⁵ Mandel, J., The Statistical Analysis of Experimental Data, Dover Publications, New York, NY, 1964.