Designation: D5280 – 96 (Reapproved 2013)

Standard Practice for Evaluation of Performance Characteristics of Air Quality Measurement Methods with Linear Calibration Functions[1]

This standard is issued under the fixed designation D5280; 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[2] covers procedures for evaluating the following performance characteristics of air quality measurement methods: bias (in part only), calibration function and linearity, instability, lower detection limit, period of unattended operation, selectivity, sensitivity, and upper limit of measurement.

1.2 The procedures presented in this practice are applicable only to air quality measurement methods with linear continuous calibration functions, and the output variable of which is a defined time average. The linearity may be due to postprocessing of the primary output variable. Additionally, replicate values belonging to the same input state are assumed to be normally distributed. Components required to transform the primary measurement method output into the time averages desired are regarded as an integral part of this measurement method.

1.3 For surveillance of measurement method stability under routine measurement conditions, it may suffice to check the essential performance characteristics using simplified tests, the degree of simplification acceptable being dependent on the knowledge on the invariance properties of the performance characteristics previously gained by the procedures presented here.

1.4 There is no fundamental difference between the instrumental (automatic) and the manual (for example, wet-chemical) procedures, as long as the measured value is an average representative for a predefined time interval. Therefore, the procedures presented are applicable to both. Furthermore, they are applicable to measurement methods for ambient, workplace, and indoor atmospheres, as well as emissions.

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:*[3]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E456 Terminology Relating to Quality and Statistics

2.2 *ISO Standard:*

ISO 6879:1983 Air Quality—Performance Characteristics and Related Concepts for Air Quality Measuring Methods[4]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this practice, refer to Terminology D1356.

3.2 *Definitions of Terms Specific to This Standard:*

NOTE 1—The statistical performance characteristics used throughout this practice are estimated, by convention, at the confidence level $1 - \alpha = 0.95$.

3.2.1 *averaging time*—predefined time interval length for which the air quality characteristic is made representative and $\Delta\theta$ the averaging time.

3.2.1.1 *Discussion*—Every measured value obtained is representative for a defined interval of time, τ, the value of which always lies above a certain minimum due to the intrinsic properties of the measuring procedure applied. In order to attain mutual comparability of data pertaining to comparable objects, a normalization to a common, predefined interval of time is necessary.

[1] This practice is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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[2] This practice was adapted from International Standard ISO/DP 9169, prepared by ISO/TC 146/SC 4/WG 4, by the kind permission of the Chairman of ISO/TC 146 and the Secretariat of ISO/TC 146/SC 4.

[3] 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.

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

3.2.1.2 *Discussion*—By convention, this normalization is achieved by transformation by means of a simple, linear, and unweighted averaging process.

(a) Series of Discrete Samples:

$$\hat{c}(\theta \mid \Delta\theta) = \frac{1}{K} \sum_{k=1}^{K} \hat{c}(\theta_0 + (k-1)\,\tau \;\mid \tau) \tag{1}$$

where:

θ_0 = $\theta - \Delta\theta$, and
$K\tau$ = $\Delta\theta$, $\tau << \Delta\theta$

(b) Continuous Time Series:

$$\hat{c}(\theta \mid \Delta\theta) = \frac{1}{\Delta\theta} \int_{\theta_0}^{\theta} d\theta \hat{c}(\theta \mid \tau) \tag{2}$$

In both cases (*a* and *b*), the original sample, described by $\hat{c}(t)$, is linked to a representative interval of time of length τ whereas $\hat{c}(\Delta\theta)$, the result after application of the averaging process, is made representative for the interval of time $\Delta\theta$ (just preceding θ), the averaging time.

3.2.1.3 *Discussion*—The averaging time, $\Delta\theta$, is therefore the predefined and, by convention, common time interval length for which the measured variable $\hat{c}$ is made representative in a sense that the square deviation of the original values, attributed to time interval lengths $\tau << \Delta\theta$ from $\hat{c}$ over $\Delta\theta$ is a minimum.

3.2.1.4 *Discussion*—The averaging process can alternatively be realized by means of a special sampling technique (averaging by sampling).

3.2.2 *continuously measuring system*—a system returning a continuous output signal upon continuous interaction with the air quality characteristic.

3.2.3 *influence variable*—a variable affecting the interrelationship between the (true) values of the air quality characteristic observed and the corresponding measured values; for example, variable affecting the slope or the intercept of or the scatter around the calibration function.

3.2.4 *noncontinuously measuring system*—a system returning a series of discrete output signals.

3.2.4.1 *Discussion*—The discretization of the output variable can be due to sampling in discrete portions or to inner function characteristics of the system components.

3.2.5 *period of unattended operation*—the maximum admissible interval of time for which the performance characteristics will remain within a predefined range without external servicing, for example, refill, calibration, adjustment.

3.2.6 *random variable*—a variable that may take any of the values of a specified set of values and with which is associated a probability distribution.

3.2.7 *randomization*—if, from a population consisting of the natural numbers 1 to *n*, these are drawn at random one by one successively without replacement until the population is exhausted, the numbers are said to be drawn in random order.

3.2.7.1 *Discussion*—If these numbers have been associated in advance with *n* distinct objects or *n* distinct operations that are then rearranged in the order in which the numbers are drawn, the order of the objects or operations is said to be randomized.

3.2.8 *reference conditions*—a specified set of values (including tolerances) of influence variables delivering representative values of performance characteristics.

3.2.9 *variance function*—a variance of the output variable as a function of the air quality characteristic observed.

3.2.10 *warm-up time*—the minimum waiting time for an instrument to meet predefined values of its performance characteristics after activating an instrument stabilized in a nonoperating condition.

3.2.10.1 *Discussion*—In practice, the warm-up time can be determined by using the performance characteristic that is expected to require the longest interval of time.

3.2.10.2 *Discussion*—In the case of the manual procedures, run-up time is used correspondingly.

3.3 *Symbols and Abbreviations:*

3.3.1 a_0, a_1, a_2—coefficients of the variance function model.

3.3.2 b_0, b_1—parameters of the estimate function for the calibration function.

3.3.3 *C*—air quality characteristic.

3.3.4 *c*—value of *C*.

3.3.5 $\hat{c}$—measured value at *c*.

3.3.6 c_i—value of *C* in the *i*-th sample; this sample may be generated from reference material.

3.3.7 c_0—normalization factor for air quality characteristics; in this case $\mid c_0 \mid = 1$.

3.3.8 Δc_I—inaccuracy of *C* at c_I.

3.3.9 $\bar{c}_\omega$—weighted mean, with set of weights ω_k.

3.3.10 $D(b_0)$—drift (see ISO 6879:1983) of the intercept of the linear calibration function.

3.3.11 $D(b_1)$—drift of the slope of the linear calibration function.

3.3.12 $D(\hat{c})$—drift of the measured value, $\hat{c}$, at *c*.

3.3.13 $DEP(b_0)_{IVi}$—first order measure of dependence of the intercept on the influence variable labeled by *i*.

3.3.14 $DEP(b_1)_{IVi}$—first order measure of dependence of the slope on the influence variable labeled by *i*.

3.3.15 $DEP(\hat{c})_{IVi}$—first order measure of dependence of the measured value on the influence variable labeled by *i* at *c*.

3.3.16 $DEP(x)_{IVi}$—first order measure of dependence of the output signal on the influence variable labeled by *i*.

3.3.17 *F*—statistic (cf *F*-test).

3.3.18 F_x—*x*-quantile of the *F*-distribution.

3.3.19 I_{IVi}— selectivity with respect to the influence variable labeled by *i*.

3.3.20 IV_i— influence variable labeled by *i*.

3.3.21 iv_i— value of IV_i.

3.3.22 $\Delta\ iv_i$—difference of values of IV_i.

3.3.23 *L*—total number of time intervals of the instability test.

3.3.24 *LDL*—lower detection limit.

3.3.25 *M*—total number of samples generated by reference material within one calibration experiment.

3.3.26 N_i— number of values of the output variable at c_i.

3.3.27 P_{lll}, p_u—estimate of the slope of the regression function of the output variable on time at $c = c_{lll}$, $c = c_u$, respectively.

3.3.28 R—reproducibility.

3.3.29 r—repeatability.

3.3.30 RES_c— resolution at $C = c$.

3.3.31 $\hat{s}$—estimate of the smoothed standard deviation of X at c.

3.3.32 $\hat{s}^2$—smoothed estimate of the variance of X (repeated measurements) at c.

3.3.33 s_0—normalization factor for the standard deviation; the magnitude of s_0 equals to 1.

3.3.34 s_{b_0}, s_{b_1}—estimate of the standard deviation of instability (see ISO 6879:1983) of the intercept and the slope of the linear calibration function.

3.3.35 sc—estimate of the standard deviation of instability at c.

3.3.36 s_i— estimate of the standard deviation of repeated x_{ij} at c_i; j repetition index.

3.3.37 $\hat{s}_i$—smoothed estimate of the standard deviation of "repeated" x_{ij} at c_i; j repetition index.

3.3.38 s_r— estimate of the repeatability standard deviation.

3.3.39 $s_{\hat{c}x}$—estimate of the standard deviation of the experimentally determined calibration function (in units of the air quality characteristic).

3.3.40 s_{xc}— estimate of the standard deviation of the experimentally determined calibration function (in units of the output variable).

3.3.41 $t_{\upsilon;q}$—q-quantile of the t-distribution with υ degrees of freedom.

3.3.42 TC—test characteristic of Grubbs' outlier test.

3.3.43 X—output variable.

3.3.44 x—value of X.

3.3.45 x—estimate of x.

3.3.46 x_i— estimate of output signal at c_i.

3.3.47 $\bar{x}_i$—mean of the set of output signals at c_i.

3.3.48 $x_{i,extr}$—output signal at c_i with the highest absolute distance from $\bar{x}_i$.

3.3.49 x_{ij}—j-th output signal at c_i.

3.3.50 $x_{l;i}$, $x_{u;i}$—output signal after i time intervals at the lower and upper value of the air quality characteristic of reference material.

3.3.51 $\bar{x}_\omega$—weighted mean of the whole set of output signals within the calibration experiment.

3.3.52 β_0, β_1—intercept and slope of the linear calibration function, respectively.

3.3.53 θ—time.

3.3.54 $\Delta\theta$—averaging time.

3.3.55 υ—number of degrees of freedom in the calibration experiment.

3.3.56 υ_1, υ_2—number of degrees of freedom for the numerator and denominator of the F-distribution, respectively.

3.3.57 $\omega = \omega(c)$—continuous weighing factor gained by modeling s_i.

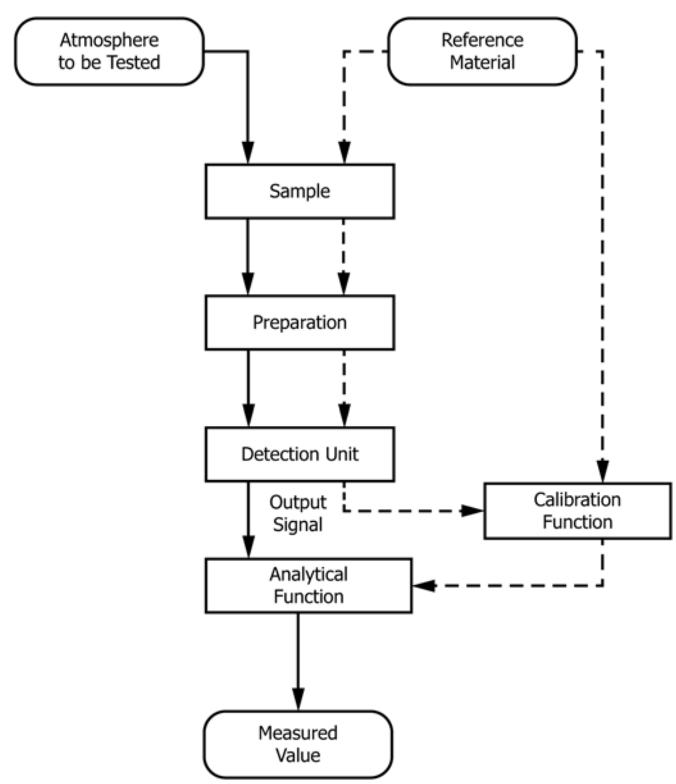
3.3.58 ω_1—weighing factor at c_1.

4. Requirements and Provisions

4.1 *Description of the Steps of the Measurement Methods Under Test*—Describe all steps of the measurement method used, such as sampling, analysis, postprocessing, and calibration. Fig. 1 illustrates schematically the steps to be followed in making a measurement or performing a series of calibration experiments in order to determine the performance characteristics.

NOTE 2—Under certain conditions it may be suitable to test only one step or a selected group of steps of the measurement method. Under other conditions it may not be possible to include all the steps of the measurement method. However, include as many steps as possible.

4.2 *Specification of Performance Characteristics to Be Tested*—Specify the performance characteristics of the measurement method in order of their relevance for the final assessment of accuracy. The descriptors of the calibration function, for example, intercept, β_0, and slope, β_1, as well as their qualifying performance characteristics are vital. Those performance characteristics for which prior knowledge is available, and those pertaining to influence variables covered by randomization are of lesser importance and need not be determined.



NOTE 1— ____Measurement Branch.

NOTE 2— _ _ _ Calibration Branch.

FIG. 1 Schematic of the Procedures of Measurement and of Evaluation for Performance Characteristics

4.3 *Test Conditions*—Perform the tests under explicitly stated conditions representative of the operational measurements. When testing for performance characteristics, describing functional dependencies, keep all influence variables constant except the one under consideration.

5. Test Procedures

5.1 *Averaging Time (see 3.2.1)*—The range of allowable averaging times is constrained by the requirement that the differences of subsequent output signals be mutually statistically independent. The corresponding minimum of the averaging time is determined by a specific performance (time) characteristic, that is, continuously measuring systems; the response time and noncontinuously measuring systems; the sample time (filling time, accumulation time, etc.).

5.1.1 *Continuously Measuring Systems*—In order to establish response time, lag time, and rise and fall time, input a step function of the air quality characteristic to the continuously measuring system. This may be done by abruptly changing the value of the air quality characteristic from, for example, 20 to 80 % of the upper limit of measurement (cf Fig. 2). Confirm these performance characteristics by an appropriate number of repetitions. If rise time and fall time differ, take the longer one for the computation of the response time. By convention the minimum averaging time equals four times the response time.

5.1.2 *Noncontinuously Measuring Systems*—Determine the minimum averaging time by the maximum of the sampling time, filling time, or accumulation time, depending on the measurement method.

5.2 *Functional and Statistical Performance Characteristics:*

5.2.1 The performance characteristics to be determined are:

5.2.1.1 Performance characteristics related to the calibration function and its stability under reference conditions, and

5.2.1.2 Performance characteristics related to the dependence of the calibration function on influence variables.

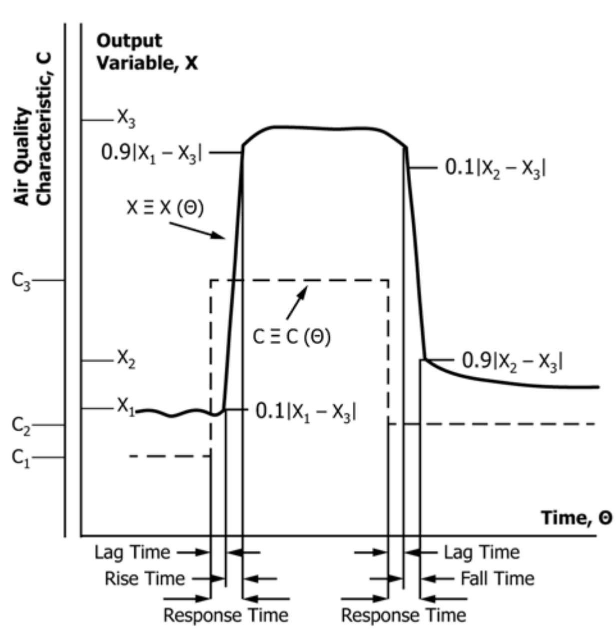


FIG. 2 Response Illustrating the Performance (Time) Characteristic of a Continuously Measuring System

5.2.2 Determine a linear calibration function by its slope (sensitivity) and its intercept. Describe instability and the effects of influence variables by their impacts on the slope (sensitivity) and intercept.

5.2.3 Obtain all output signals evaluated throughout these tests after the measuring system has reached stabilized conditions.

5.3 *Calibration:*

5.3.1 A calibration experiment for the evaluation of performance characteristics consists of at least ten repeated measurements at a minimum of five different values (two each) of the air quality characteristic.

5.3.2 In case of drift, restrain the duration of the calibration experiment to one as short as possible. This may be accomplished by consecutive instrument readings at a certain value of the air quality characteristic and after a change of that value and stabilization, again consecutive instrument readings at that value, etc. (see Fig. 3). This is only valid in the absence of hysteresis or if hysteresis is negligible.

NOTE 3—Repetitions performed under reproducibility conditions (see Practice E177) require a random sample of the population of the influence variables to be examined (randomization).

5.3.3 *Elimination of Outliers*—Usually, experience helps to identify potential outliers. A less arbitrary way of detection of such potential outliers is given by combination of this experience with, for example, Grubbs' test (**1**).[5] However, it should be clear that such a test identifies potential outliers. The underlying reasons may be statistical or due to system operation interferences. The latter presents a sufficient foundation for the elimination of the respective output signal (confirmation as an outlier).

5.3.3.1 Estimate the standard deviation s_i at c_i by the following:

$$s_i = \sqrt{\frac{N_i \sum_j x_{ij}^2 - \left(\sum_j x_{ij}\right)^2}{(N_i - 1)}} \quad (3)$$

At c_i, take the output signal with the highest absolute distance from the mean output signal $\bar{x}_1$. Derive the test characteristic as follows and compare it with the tabulated value of Grubbs' two-sided outlier test (see Annex A1) to be taken as the critical value:

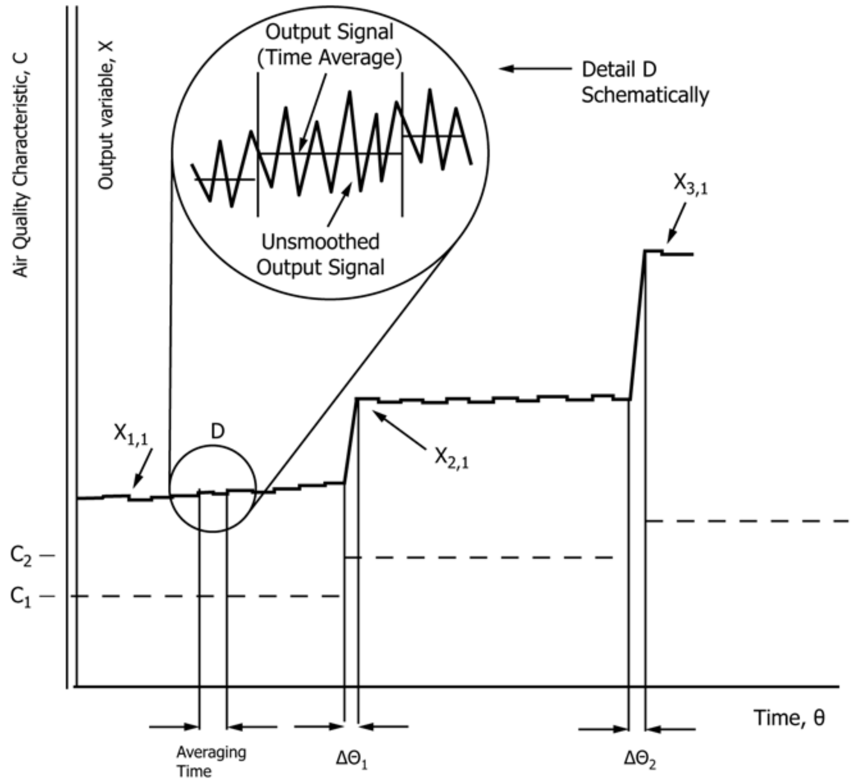
$$TC = \frac{\left| x_{i,extr} - \bar{x}_i \right|}{s_i} \quad (4)$$

where:

$$\bar{x} = \frac{\sum_j x_{ij}}{N_i} \quad (5)$$

5.3.3.2 If *TC* exceeds the critical value, check if it is due to operational reasons, and if so, reject it. This procedure may be repeated; however, no more than 5 % of the number of output signals may be rejected this way. Otherwise this calibration experiment is not valid.

[5] The boldface numbers in parentheses refer to the list of references at the end of the text.



NOTE 1—X_{ij}—j-th time average over the interval of time Δθ at the *i*-th value of the air quality characteristic generated by reference material.
$\Delta\theta_i$—Intervals of time during which unsmoothed output signals shall not be submitted to the averaging procedure, and thus, not be evaluated.

FIG. 3 Example of a Calibration Experiment

5.3.3.3 If operational reasons are not found for T_c exceeding the critical value, the potential outlier may not be rejected. In this case, validate the basic test assumptions and prerequisites.

5.3.4 *Computation of the Variance Function*—The variance function is the central tool for the estimation of relevant performance characteristics. Therefore, some instructions for its computations and the computation of related parameters, are described as follows:

5.3.4.1 Compute the variance s_i^2 of the output signals x_{ij} ($j = 1$ to N_i) for each of the values c_i ($i = 1$ to M) of the air quality characteristic as follows:

$$s_i^2 = \frac{N_i \sum_j x_{ij}^2 - \left(\sum_j x_{ij}\right)^2}{N_i - 1} \quad (6)$$

Additionally, determine the dependence of s_i^2 on c using the following:

$$\log \frac{s^2}{s_0^2} \approx a_0 + a_1 \sqrt{\frac{c}{c_0}} + a_2 \left(\sqrt{\frac{c}{c_0}}\right)^2 \quad (7)$$

Compute the coefficients of this non-weighted second order polynomial in $\sqrt{(c / c_0)}$ as follows:

$$a_0 = \frac{\sum_i y_i - a_1 \sum_i z_i - a_2 \sum_i z_i^2}{M} \quad (8)$$

$$a_1 = \frac{Q_{(z,y)} Q_{(z^2,z^2)} - Q_{(z^2,y)} Q_{(z,z^2)}}{Q_{(z,z)} Q_{(z^2,z^2)} - \left(Q_{(z,z^2)}\right)^2} \quad (9)$$

$$a_2 = \frac{Q_{(z^2,y)} Q_{(z,z)} - Q_{(z,y)} Q_{(z,z^2)}}{Q_{(z,z)} Q_{(z^2,z^2)} - \left(Q_{(z,z^2)}\right)^2} \quad (10)$$

with

$$Q_{(\zeta^m,\eta^n)} = \frac{\sum_i \left(\zeta_i^m \eta_i^n\right) - \left(\sum_i \zeta_i^m\right)\left(\sum_i \eta_i^n\right)}{M} \quad (11)$$

Obtain element $Q(\zeta m,\eta n)$ by substituting ζ by z and η by z or y as follows:

$$y_1 = \log \frac{s_i^2}{s_0^2} \quad (12)$$

$$z_1 = \sqrt{\frac{c_1}{c_0}} \quad (13)$$

5.3.4.2 An example of a variance function obtained this way is shown in Fig. 4.

5.3.4.3 Consequently, obtain the smoothed variance function, $\hat{s}^2$, as follows:

$$\hat{s}^2 = \hat{s}^2(c) = s_0^2 \exp\left(a_0 + a_1 \sqrt{\frac{c}{c_0}} + a_2 \frac{c}{c_0}\right) \quad (14)$$

5.3.4.4 The weighting factor ω_i at c_i ($i = 1$ to M) to be used later on in the computation of the calibration function **(1-3)** is proportional to the inverse of the above variance:

$$\omega = \omega(c) = \frac{s_0^2}{\hat{s}^2} \quad (15)$$

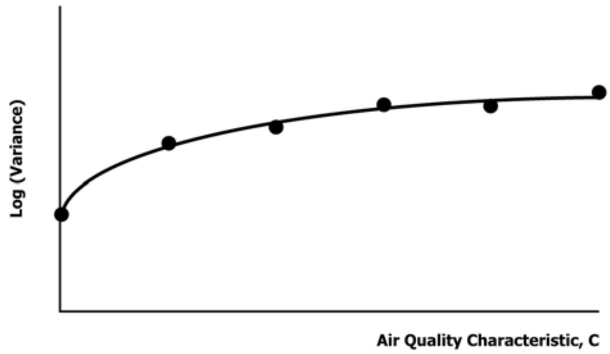


FIG. 4 Fit of the Logarithm of the Variance Function

5.3.5 *Computation of the Calibration Function*—Estimate a linear calibration function (**4**) as follows (Eq 15):

$$x = \beta_o + \beta_1 c \tag{16}$$

may be estimated by:

$$x = b_0 + b_1 c \tag{17}$$

where:

$$b_0 = \bar{x}_\omega - b_1 \bar{c}_\omega \tag{18}$$

$$\bar{c}_\omega = \frac{\sum_i N_i \omega_i c_i}{\sum_k N_k \omega_k} \tag{19}$$

$$\bar{x}_\omega = \frac{\sum_i \sum_j \omega_i x_{ij}}{\sum_k N_K \omega_k} \tag{20}$$

$$b_1 = \frac{\sum_i \sum_j \omega_i x_{ij} (c_i - \bar{c}_\omega)}{\sum_1 N_i \omega_i (c_i - \bar{c}_\omega)^2} \tag{21}$$

5.3.5.1 Additionally, to the various standard deviations designated as descriptors for the mutual scattering of accepted true values, measured values, and output signals, there arises a special scatter to be attributed to the estimation process outlined as a whole.

5.3.5.2 This scatter may be described by the following standard deviation (**2**):

$$s_x c = \sqrt{\frac{\sum_{i=1}^{M} \omega_i \sum_{k=1}^{N_i} (x_{ik} - x_i)^2}{\left[\sum_{i=1}^{M} (N_i)\right] - 2}} \tag{22}$$

5.3.5.3 Sometimes the output signal is obtained after correction for the blank. The corrected calibration function must pass through the origin if the blanks correspond to genuine zero samples. In this case the coefficient, b_1, reduces to the following:

$$b_{i:trf} = \frac{\sum_i \sum_j \omega_i x_{ij} c_i}{\sum_k N_k \omega_k c_k^2} \tag{23}$$

5.3.5.4 The standard deviation, $s_x c$, is invariant to the transformation, only the number of degrees of freedom changes to the following:

$$V_{trf} = \left(\sum_{i=1}^{M} N_i\right) - 1 \tag{24}$$

5.3.6 *Computation of the Analytical Function*—Compute the analytical function by inverting the calibration function as follows:

$$\hat{c} = \frac{x - b_0}{b_1} \tag{25}$$

5.3.7 *Linearity*—Test the hypothesis of linearity of the calibration function (see Fig. 5) using the statistic F (**4**) as

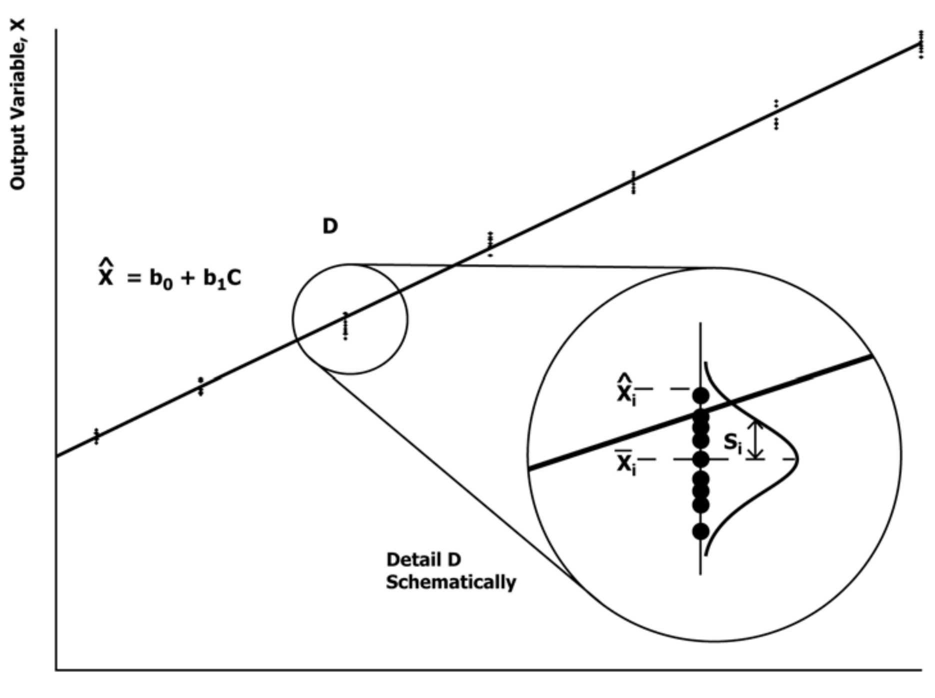


FIG. 5 Nonlinear Calibration Function: Hypothesis of Linearity Rejected

follows:

$$F = \frac{\frac{\sum_i N_i \omega_i (\bar{x}_i - x_i)^2}{v_1}}{\frac{\sum_i \sum_j \omega_i (x_{ij} - \bar{x}_i)^2}{v_2}} \quad (26)$$

where:

$$v_1 = M - 2 \quad (27)$$

$$v_2 = \sum_i (N_1 - 1) \quad (28)$$

5.3.8 If F does not exceed the tabulated value, $F_{v_1;v_2;1-\alpha}$, of the F-distribution for the one-sided test for the significance level $\alpha = 0.05$ (see Annex A1) to be taken as a critical value, nonlinearity is negligible. Determine the subsequent performance characteristics as shown.

5.3.9 If F exceeds the critical value, reject the hypothesis of linearity. Determine whether nonlinearity is substantial as compared to other uncertainties by determining if the following inequality criterion holds:

$$\underset{i=1}{\overset{M}{MAX}} \left\{ \frac{|\bar{x}_i - x_i|}{2s_i} \right\} < 1 \quad (29)$$

5.3.10 If the inequality criterion is not fulfilled (see Fig. 5), terminate the procedure of determining the performance characteristics. For the latter situation, perform the following steps and measures:

5.3.11 Examine the quality of the reference material samples as a potential cause for nonlinearity. If, based on the result of this examination, the problem cannot be solved, examine whether the sub-range where the inequality criterion is fulfilled contains the region of interest, or test for a monotonic transformation with a monotonic first derivative to reduce the deviation from linearity. If the possibility of reducing the deviation from linearity is accepted, then a definition of a new measurement method requiring a new test for determination of performance characteristics is required.

5.3.12 *Uncertainty Due to Estimating the Calibration Function*—The coefficients b_0 and b_1 of the calibration function are estimates obtained from a limited number of measurements. They will, thus, deviate from the true values which would be obtained with a complete set. Therefore, any estimated measure value, $\hat{c}$, obtained by means of the calibration function, will deviate from the "accepted true" value. This deviation will change at random whenever the measuring system is calibrated.

5.3.13 Describe **(3)** the uncertainty of the measured value, $\hat{c}$, under the calibration experiment performed, by the estimate $s_{\hat{c}x}$ for the respective standard deviation (cf. 5.3.5):

$$s_{\hat{c}x} = \frac{s_{xc}}{b_1} \sqrt{\frac{1}{\sum_i N_i \omega_i} + \frac{(c - \bar{c}_\omega)^2}{\sum_i N_i \omega_i (c_i - \bar{c}_\omega)^2}} \quad (30)$$

5.3.14 For a simplified two-point field calibration, assuming the performance characteristics evaluated remain stable, use the following approximation formula:

$$s_{\hat{c}x} \approx \frac{1}{b_1} \sqrt{\left(1 - \frac{c}{c_{sp}}\right)^2 \hat{s}^2(0) + \left(\frac{c}{c_{sp}}\right)^2 \hat{s}^2(c_{sp})} \quad (31)$$

with the reference materials at:
$C = 0$ (zero sample) and
$C = c_{sp}$ (span sample).

5.4 *Precision:*

5.4.1 *Repeatability*—Calculate the repeatability r using the variance functions referring to the corresponding conditions (see Terminology E456).

5.4.1.1 Calculate the smoothed variance function $\hat{s}^2(c)$, (see 5.3.4) and therefrom, estimate the repeatability standard deviation by the following:

$$s_r = \frac{\sqrt{\hat{s}^2(c)}}{b_1} \quad (32)$$

5.4.1.2 Compute the repeatability, r, from the following:

$$r = t_{v;0.975} s_r \sqrt{2} \quad (33)$$

where:

$t_{;0.975}$ is the tabulated value $t_{v;1-\alpha/2}$ of the t-distribution for the two-sided test for the significance level $\alpha = 0.05$ (see Annex A3), and for ν degrees of freedom:

$$\nu = MIN\{N_i - 1\}. \quad (34)$$

1

NOTE 4—$\sqrt{2}$ originates from the fact that r and R, as determined by definition, refer to the difference between two single measurements.

5.4.2 *Measurement Resolution*—Estimate the measurement resolution at $C = c$ by the following:

$$RES_c = \frac{t_{v;0.95} \hat{s}_c \sqrt{2}}{b_1} \quad (35)$$

5.4.3 *Lower Detection Limit:*

5.4.3.1 Calculate the variance, $\hat{s}^1(0)$, at $C = 0$ from the variance function (5.3.4). The repeatability standard deviation is then, in accordance with 5.4, as follows:

$$s_r = \frac{\sqrt{\hat{s}^2(0)}}{b_1} \quad (36)$$

5.4.3.2 For reference conditions of operation, the lower detection limit (LDL) becomes:

$$LDL = t_{v;0.95} \sqrt{s_r^2 + s_{\hat{c}x;}^2} \; (s_r \text{ and } s_{\hat{c}x} \text{ at } C = 0) \quad (37)$$

5.4.4 *Upper Limit of Measurement*—Approximate the upper limit of measurement by the value of the air quality characteristic corresponding to the maximum measured value confirmed by the calibration process.

NOTE 5—For methods featuring signal averaging, the operational upper limit of measurement will be lower depending upon the fluctuations of the value of the air quality characteristic within the averaging period.

5.4.5 *Instability:*

5.4.5.1 Performance characteristics are assumed not to change with time. However, in practice they do. In particular, the change of the coefficients b_0 and b_1 of the calibration function may have a considerable influence on the accuracy of the measured value. The change of the coefficients over a stated period of time (instability) may have a systematic part (drift) and a random part (dispersion). It is assumed that the value of drift is a constant. The value of the dispersion standard deviation is equal to or greater than the repeatability standard deviation.

5.4.5.2 Drift and dispersion are derived from the linear regression of the output variable over time, where the time interval between successive output signals is the time interval of interest (Fig. 6). Drift is equal to the slope of the regression function, and the dispersion is measured by the standard deviation of the residuals.

5.4.5.3 Select the interval of time, Δθ, over which instability shall be tested, for example, the interval of time between successive calibrations.

5.4.5.4 Use reference material of $C = c_t$ and $C = c_u$ (c_t in the lower and c_u in the upper part of the range of measurement; $c_t << c_u$).

5.4.5.5 At θ = 0 sample at $C = c_t$. Record the corresponding output signal $x_{l;0}$. Sample at $C = c_u$. Record the corresponding output signal $x_{u;0}$. Repeat this process L times ($L \geq 8$), equidistant in time Δθ.

5.4.5.6 Compute the drift p_ι and the dispersion standard deviation, s_t, for $C = c_t$, as follows:

$$p_{|fl} = \frac{\sum_i \theta_i x_{|fl;i} - \left(\sum_i \theta_i\right)\left(\sum_i x_{|fl;i}\right)/L}{\sum_i \theta_i^2 - \left(\sum_i \theta_i\right)^2/L} \tag{38}$$

$$s_{|fl} = \sqrt{\frac{1}{L-2}\sum_1 \left[x_{|fl;i} - \bar{x}_{|fl} - p_{|fl}\left(\theta_i - \bar{\theta}\right)\right]^2} \tag{39}$$

Compute the corresponding values of p_u and s_u for $C = c_u$.

5.4.6 *Drift:*

5.4.6.1 Express the drift as a time change of b_0 and b_1 of the calibration curve:

$$D(b_0) = \frac{\Delta b_0}{\Delta\theta} = \frac{c_{|fl} p_u - c_u p_{|fl}}{c_{|fl} - c_u} \tag{40}$$

$$D(b_1) = \frac{\Delta b_1}{\Delta\theta} = \frac{p_u - p_{|fl}}{c_u - c_{|fl}} \tag{41}$$

5.4.6.2 It follows then, that at any value $C = c$ in the range considered, the estimated drift becomes:

$$D(\hat{c}) = \frac{\Delta c}{\Delta\theta} = \frac{1}{b_1} = \left[D(b_0) + cD(b_1)\right] \tag{42}$$

5.4.7 *Dispersion*—Develop the standard deviations of b_0 and b_1 under the assumption $c_u/c_\iota > s_u/s_\iota \geq 1$:

$$s_{b_0} = \sqrt{\frac{c_u^2 s_{|fl}^2 - c_{|fl}^2 s_u^2}{c_u^2 - c_{|fl}^2}} \tag{43}$$

$$s_{b_1} = \sqrt{\frac{s_u^2 - s_1^2}{c_u^2 - c_1^2}} \tag{44}$$

5.4.7.1 Finally, the dispersion part of instability to be expected is:

$$s_{inst} = \frac{1}{b_1}\sqrt{s_{b_0}^2 + c^2 s_{b_1}^2} \tag{45}$$

5.4.7.2 If this dispersion does not exceed the respective repeatability standard deviation, long-term fluctuations are negligible in the interval of time, Δθ, evaluated.

5.5 *Dependence of the Measured Value on Influence Variables*—This test is designed to estimate the performance retained under field conditions. It is assumed that the impact of the influence variable on the measured value can be fairly determined by tests at the extremes (see Fig. 7). Divide the influence variables into classes of known and unknown effect on the measured value. Examples of the first class are temperature and pressure as long as a classical gas state equation remains valid. Usually, however, the relationship is more complicated and is unknown, for example, the effects of

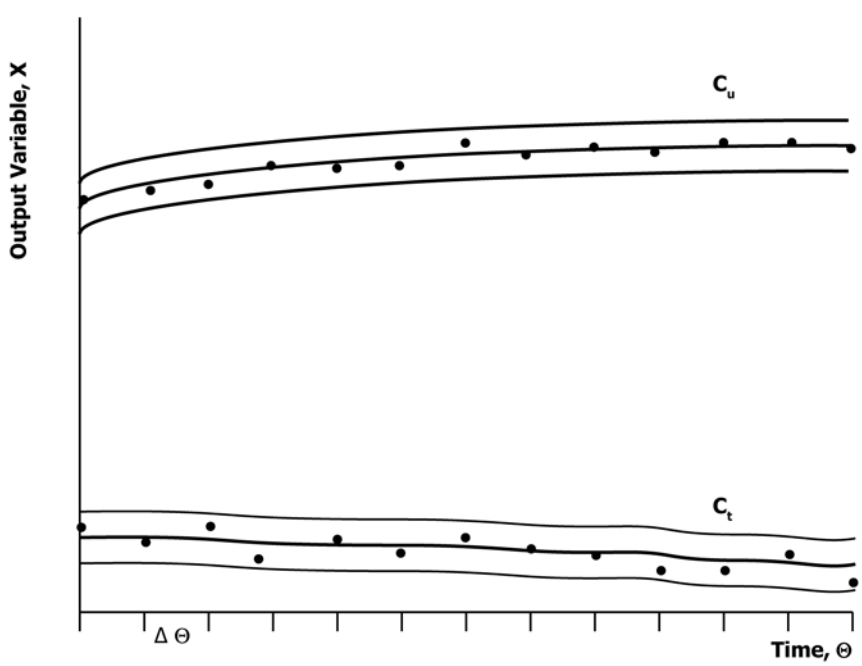


FIG. 6 Example of Instability Test

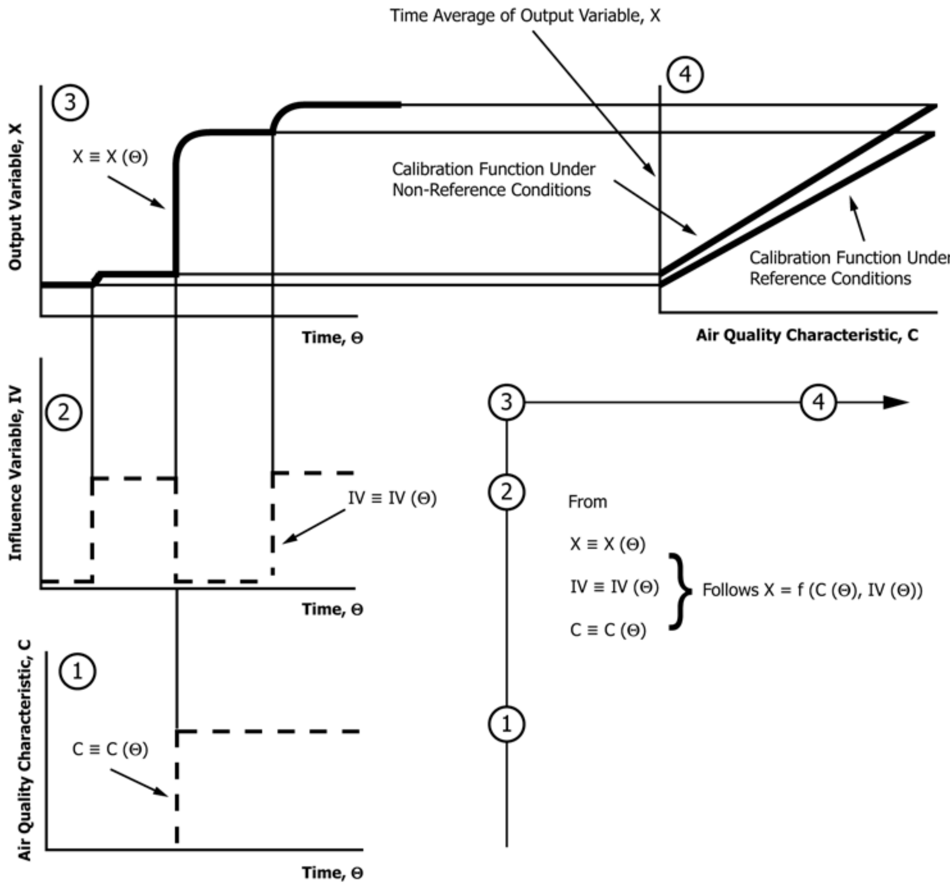


FIG. 7 Impact of an Influence Variable on a Linear Calibration Function Illustrated for the Case of a Two-Point Calibration

temperature by means of electronics, those due to line voltage, and interferant concentrations.

5.5.1 *Known Dependence*—Express the measured value, $\hat{c}$, as a function of the air quality characteristic and the *i*-th influence variable, IV_i: $\hat{c} = g(C, IV_1 \ldots, IV_k)$.

5.5.1.1 Approximate the dependence, DEP, on IV_i at $C = c$ by the following corresponding partial derivative:

$$DEP(\hat{c})_{IV_i} = \frac{\partial g}{\partial (IV_i)} \mid c, iv_1 \ldots iv_k \quad (46)$$

5.5.2 *Unknown Dependence*—Use reference material of $C = c_1$ and $C = C_u$ (c_ι in the lower and c_u in the upper part of the measurement range; $c_\iota << c_u$).

5.5.2.1 In order to determine experimentally the dependence on the influence variable, perform tests at the operational extremes of the influence variable, and under reference conditions for the remaining influence variables, as follows:

5.5.2.2 Record for each of the values of C the difference in output signal, Δx, going from the one extreme test value, IV_i, to the other.

5.5.2.3 Compute the dependence, *DEP*, on the influence variable, IV_i, at $C = c_k$, $k = \iota, \mu$:

$$DEP(x)_{IV_i} = \frac{\Delta x}{\Delta iv_i} \mid C = c \quad (47)$$

5.5.2.4 The dependence of b_0 and b_1 on the influence variable is shown by the following:

$$DEP(b_0)_{IV_i} = \frac{c_u DEP(x)_{IV_i \mid c_{|fl}} - c_{|fl} DEP(x)_{IV_i \mid c_u}}{c_u - c_{|fl}} \quad (48)$$

$$DEP(b_1)_{IV_i} = \frac{DEP(x)_{IV_i \mid c_u} - DEP(x)_{IV_i \mid c_{|fl}}}{c_u - c_{|fl}} \quad (49)$$

5.5.2.5 At any value $C = c$ in the range considered, the estimated dependence of the measured value on influence variable IV_i becomes:

$$DEP(\hat{c})_{IV_i} = \frac{1}{b_1}\left[DEP(b_0)_{IV_1} + cDEP(b_1)_{IV_i}\right] \quad (50)$$

5.5.2.6 In accordance with ISO 6879:1983, a first order approximation for the selectivity, I, with respect to IV_i is shown by the following:

$$I_{IV_i} = b_1 \frac{\Delta iv_i}{\Delta x} \quad (51)$$

5.6 *Operational Performance Characteristics:*

5.6.1 *Warm-Up Time; Run-Up Time*—Investigate the performance characteristic that probably will be the limiting factor in time. Examples are lower detection limit and repeatability.

5.6.2 Investigate the most unfavorable operating conditions to be expected. Test at those conditions. If the measuring system was operating, return to a nonoperating condition. Wait until the measuring system becomes stable. Initiate the measuring system. Determine the time elapsed to reach the given range of the chosen performance characteristic.

5.6.3 *Period of Unattended Operation*—Refer to the limit value of the performance characteristics taking into account, in analogy with 5.6.1, and investigate the critical performance characteristic limiting the period of unattended operation.

5.6.3.1 Investigate the most unfavorable operating conditions to be expected.

5.6.3.2 Perform the necessary maintenance operations.

5.6.3.3 Initiate the measuring system in accordance with the operating instructions at the most unfavorable operation conditions and allow the measuring system to achieve warmed up or run up conditions. Record the time elapsed until stabilization has been established.

5.6.3.4 Operate the measuring system without intervention.

5.6.3.5 Check the value of the limiting performance characteristic regularly until it is not within its limits.

5.6.3.6 Record the time elapsed through the last positive check. Designate this as the period of unattended operation.

5.6.3.7 Otherwise repeat the test several times or test with various measuring systems. The minimum period in the set elapsed until the first negative check is the general period of unattended operation.

5.6.3.8 Report the period of unattended operations together with the admissible ranges of the performance characteristics.

6. Keywords

6.1 bias; calibration function; instability; linearity; lower detection limit; period of unattended operation; selectivity; sensitivity; upper limit of measurement

ANNEXES

(Mandatory Information)

A1. TABULATED VALUES OF GRUBBS' TWO-SIDED OUTLIER TEST

TABLE A1.1 Tabulated Values of Grubbs' Two-Sided Outlier Test

NOTE 1—For the significance level $\alpha = 10^{A}$.

Number of Replicates	Tabulated Value (Critical Value) (TC)
3	1.155
4	1.481
5	1.715
6	1.887
7	2.020
8	2.125
9	2.215
10	2.290
11	2.355
12	2.412
13	2.462
14	2.507
15	2.549
16	2.585
17	2.620
18	2.651
19	2.681
20	2.709
25	2.822
30	2.908
40	3.036
50	3.128

A2. TABULATED VALUES $F_{\upsilon 1,\upsilon 2;1-\alpha}$ of the F-DISTRIBUTION

TABLE A2.1 Tabulated Values $F_{\upsilon 1,\upsilon 2;1-\alpha}$ of the *F*-Distribution for the One-Sided Test

NOTE 1—For the significance level $\alpha = 0.05$.

	Number of degrees of freedom of variance in the numerator υ_1[A]											
*)[B]	1	2	3	4	5	6	7	8	9	10	11	12
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12	2.08	2.04	2.00
50	4.03	3.18	2.79	2.56	2.40	2.29	2.20	2.13	2.07	2.03	1.99	1.95
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04	1.99	1.95	1.92
100	3.94	3.09	2.70	2.46	2.31	2.19	2.10	2.03	1.97	1.93	1.89	1.85
120	3.92	3.07	2.68	2.45	2.29	2.18	2.09	2.02	1.96	1.91	1.87	1.83
α	3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.79	1.75

[A] Values $F_{\upsilon 1,\upsilon 2;0.95}$ for $\upsilon_1 > 30$ can also be obtained from $F_{\upsilon 1,\upsilon 2;0.95} = 10$ A
where:

$$A = \frac{1.4287}{\sqrt{\frac{2_{\upsilon_1\upsilon_2}}{(\upsilon_1+\upsilon_2)}-0.95}} - \frac{0.681\,(\varepsilon_2-\varepsilon_1)}{\varepsilon_1\,\varepsilon_2} \qquad \text{(A2.1)}$$

[B] *) denominator υ_2.

A3. TABULATED VALUES OF THE *t* -DISTRIBUTION

TABLE A3.1 Tabulated Values of the *t* -Distribution[A]

NOTE 1—For the significance level $\alpha = 0.05$.

Number of Degrees of Freedom υ	One-Sided Case $t_{\upsilon;1-\alpha} = t_{\upsilon;0.95}$	Two-Sided Case $t_{\upsilon;1-\alpha/2} = t_{\upsilon;0.975}$
1	6.314	12.706
2	2.920	4.303
3	2.353	3.182
4	2.132	2.776
5	2.015	2.751
6	1.943	2.447
7	1.895	2.365
8	1.860	2.306
9	1.833	2.262
10	1.812	2.228
11	1.796	2.201
12	1.782	2.179
13	1.771	2.160
14	1.761	2.145
15	1.753	2.131
16	1.746	2.120
17	1.740	2.110
18	1.734	2.101
19	1.729	2.093
20	1.725	2.086
30	1.697	2.042
40	1.684	2.021
60	1.671	2.000
α	1.645	1.960

[A] Values $t_{\upsilon n;0.95}$ for $\upsilon > 3$ can also be obtained from:

$$t_{\upsilon;0.95} = \frac{1.6449\upsilon + 3.5283 + \frac{0.85602}{\upsilon}}{\upsilon + 1.2209 - \frac{1.5162}{\upsilon}} \quad \text{(A3.1)}$$

values $t_{\upsilon;0.975}$ for $\upsilon > 3$

as well as from:

$$t_{\upsilon;0.975} = \frac{1.9600\upsilon + 0.60033 + \frac{0.95910}{\upsilon}}{\upsilon - 0.90259 + \frac{0.11588}{\upsilon}} \quad \text{(A3.2)}$$

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