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**NOMENCLATURE FOR THE PRESENTATION OF
RESULTS OF CHEMICAL ANALYSIS**

(IUPAC Recommendations 1994)

Prepared for publication by

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Nomenclature for the presentation of results of chemical analysis (IUPAC Recommendations 1994)

Synopsis

Reporting of the data resulting from chemical analysis constitutes the critical, final stage of the analytical process. This document has been prepared with the objective of presenting nomenclature which is both statistically and chemically appropriate to this process. The terminology and formulation have been drawn in part from ISO Standard ISO 3534 ["Statistics - Vocabulary and Symbols"] as well as other references cited at the end of this document.

The scope of the document encompasses three primary topics: (1) general terminology relating to the precision and accuracy of experimental results; (2) descriptive statistics appropriate for univariate analysis of chemical measurements, such as various measures of central value and dispersion, and formulae for calculating confidence intervals; (3) quantities employed in the estimation and application of linear calibration functions. The third topic depends on the first two for its logical development; and it provides terminology and expressions suitable for the reporting of calibration function parameters and their uncertainties, plus estimates and confidence intervals for both dependent and independent variables.

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1. INTRODUCTION

The value of much published research work on chemical analysis is diminished by the lack of a generally accepted system of reporting numerical results. It is not always feasible for a research worker to plan collaborative work for statistical study or, indeed, to carry out more than a short series of replicate determinations in his own laboratory. In the development of a new analytical method, synthetic samples or reference materials of known composition are normally used to test the proposed method, and it is generally assumed that the materials are homogeneous and that sampling errors are negligible. The results of chemical analyses under such considerations are, however, amenable to simple statistical treatment.

The text that follows is designed to provide the necessary means for reporting results in a standardized form with the intention that, by using recommended terms and symbols, an author may report his data unambiguously, without further explanation of terminology or method of computation. Only if other terms were used would it be necessary for the author to define his meaning.

The list includes both standard statistical terms, like "median," and less standardized terms, like "percentage relative error," which are useful to the analytical chemist. Such non-standardized terms, despite common use, frequently cause confusion because differing meanings are attributed to them. The statistical terms in this document have been selected and defined according to the practical needs of the laboratory analyst. Those unfamiliar with elementary statistics may find it useful to consult an introductory text, such as one of those in the list of references.

In the following text, the terms and definitions marked with an asterisk have been taken partly or wholly from the ISO Standard ISO 3534 (1993) on "Statistics - Vocabulary and Symbols."

1.1 Assumptions and Caveats. It is extremely important to realize that assumptions play a central role in the validity of the conclusions resulting from statistical operations on experimental data. Since such assumptions are frequently implicit, it is appropriate at the beginning of this document to call attention to their existence and importance. The principal assumptions of concern here relate to the model employed. For example, if we represent the observations y by the following relation,

$$y = f(x) + e,$$

we must be aware of assumptions connected with the functional relation $f(x)$, as well as those connected with the error structure e . In section 3 of this report, $f(x)$ is taken as the population mean of x -- i.e., the expected value of the observations equals a constant; in section 4, $f(x)$ is taken as $a + bx$ -- i.e., the straight line ("linear") calibration curve. Deviations from these assumed functional relations *will* result in erroneous conclusions. There are, fortunately, test statistics such as t and χ^2 and F , plus methods such as residual analysis and control charts to aid in detecting model errors, but these must not be blindly relied upon. That is because all statistical tests have two fundamental limitations: (1) they themselves rest on assumptions, and (2) their statistical power to detect erroneous models (or alternative hypotheses) is always limited -- i.e., non-detectable model error may nevertheless cause important conclusion errors. For more detailed discussion of the foundations of hypothesis testing and the relation between statistical power and significance testing (of the null hypothesis), the reader should consult a basic text on statistics.

Assumptions related to e , include: randomness, independence, homogeneity of variance (homoscedasticity), and the form of the error distribution (cdf = cumulative distribution function). For most of the discussion in this document, we assume the Normal distribution of errors. Just as in the case of the assumed functional relation, one may apply statistical tests -- such as the sign test, χ^2 , Kolmogorov-Smirnov test, etc. -- to detect deviations from the assumed error model. However, the same forementioned limitations apply. In fact, the power of distributional tests suffers seriously unless the number of degrees of freedom is very large.

We must conclude that the scientific user of statistical measures must bear full responsibility for the validity of the assumptions made, making appropriate statistical tests of the more crucial assumptions, but realizing that passing such tests does not *prove* assumption validity. When the functional relation (model) is wrong, estimates of means and calibration parameters will be biased; when the error model is wrong, presumed confidence intervals and tests of significance may be misleading. The *only* route to the correct model is through sound, scientific knowledge of the measurement process.

2. GENERAL TERMS

2.1 Measured Value. The observed value of weight, volume, meter-reading or other quantity, found in the analysis of a material.

2.2 Result. The final value reported for a measured or computed quantity, after performing a measuring procedure including all subprocedures and evaluations.

2.3 Variable. The quantity or characteristic measured or computed; see also dependent and independent variables (4.3, 4.4). The corresponding numerical value may be taken for statistical handling; it may, for example, be a measured value or result. Symbol: x .

Comment: Note that statistical usage employs capital letters for random variables, and lower case for particular or observed values. In circumstances where the choice of " x " as the symbol may cause confusion, another symbol may be used.

2.4 Series. A number of measured values ($x_1, x_2, \dots, x_i, \dots, x_n$) equivalent to each other with respect to statistical considerations, e.g., the results of repeated analyses using only one analytical method on a substance that is presumed to be homogeneous.

*2.5 **True Value.** The value that characterizes a quantity perfectly defined in the conditions that exist when that quantity is considered. It is an ideal value which could be arrived at only if all causes of measurement error were eliminated, and the entire population was sampled. Symbol: τ .

*2.6 **Accuracy.** The closeness of agreement between a test result and the true value. *Accuracy*, which is a qualitative concept, involves a combination of random error components and a common systematic error or bias component (3.14).

*2.7 **Precision.** The closeness of agreement between independent test results obtained by applying the experimental procedure under stipulated conditions. The smaller the random part of the experimental errors which affect the results, the more precise the procedure. A measure of precision (or imprecision) is the standard deviation (cf. 3.7–3.9).

Comment: As recognized in the International vocabulary of basic and general terms in metrology (ISO,1993), precision is sometimes misused for accuracy (definition 3.5). This problem will be avoided if one recognizes that precision relates only to dispersion, not to deviation from the (conventional) true value. An excellent recommendation, presented in the statistical handbook Experimental Statistics (Natrella, 1963), defines imprecision as "the standard error of the reported value."

When the performance of a method is of particular interest, the following two measures of precision are employed.

*2.8 **Repeatability.** The closeness of agreement between independent results obtained with the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratory and after short intervals of time). The measure of repeatability is the standard deviation qualified with the term: "repeatability" as repeatability standard deviation.

In some contexts repeatability may be defined as the value below which the absolute difference between two single test results obtained under the above conditions, may be expected to lie with a specified probability.

*2.9 **Reproducibility.** The closeness of agreement between independent results obtained with the same method on identical test material but under different conditions (different operators, different apparatus, different laboratories and/or after different intervals of time). The measure of reproducibility is the standard deviation qualified with the term "reproducibility" as reproducibility standard deviation.

In some contexts reproducibility may be defined as the value below which the absolute difference between two single test results on identical material obtained under the above conditions, may be expected to lie with a specified probability.

Note that a complete statement of reproducibility requires specification of the experimental conditions which differ.

3. QUANTITIES RELATED TO REPLICATE MEASUREMENTS

When reporting results obtained by replicate measurements the following quantities should be included: the number of observations (3.1), the arithmetic mean (3.4), the standard deviation (3.7), [or the range (3.6), see the comments to both terms], the confidence limits (3.15) with the level of significance or confidence level (3.3), and, if known, the true value (2.5), and the estimated bounds for bias (3.14). Other quantities reported occasionally, are also included in the following section.

*3.1 **Number of Observations.** The total number of observed data (measured values) in the series; sample size. Symbol: n .

Comment: This number should *always* be reported. In the case where an entire population can be specified, its size is denoted by N .

3.2 Degrees of Freedom. A statistical quantity indicating the number of values which could be arbitrarily assigned within the specification of a system of observations. Symbol: ν . For simple replication, with n measurements and one estimated parameter (the mean), $\nu = n - 1$.

More generally, for multivariable computations, the number of degrees of freedom equals the number of observations minus the number of fitted parameters (see section 4.).

***3.3 Confidence Level.** The probability of covering the expected value of an estimated parameter with an interval estimate for that parameter. (Symbol $1 - \alpha$.) The confidence level can be expressed as a number between 0 and 1, or in percent.

The complementary quantity α is known as the **Significance Level**.

Comment: In some cases the Confidence Level is dictated by the needs of the situation. In all other instances, use of $1 - \alpha = 0.95$ is recommended.

***3.4 Arithmetic Mean (Average).** The sum of a series of observations divided by the number of observations. Symbol: \bar{x} . It can be calculated by the formula:

$$\bar{x} = \frac{\sum x_i}{n}$$

Comment: All summations (here and later, unless otherwise stated) are taken from 1 to n . Note that the arithmetic mean is an unbiased estimate of the Population Mean μ . That is, μ is the limiting value for \bar{x} , as $n \rightarrow \infty$.

3.4.1 Weighted Mean. If in a series of observations a statistical weight (w_i) is assigned to each value, a weighted mean \bar{x}_w can be calculated by the formula:

$$\bar{x}_w = \frac{\sum w_i x_i}{\sum w_i}$$

Comment: Unless the weights can be assigned objectively, the use of the weighted mean is not normally recommended.

3.5 Deviation. The difference between an observed value and the arithmetic mean of the set to which it belongs. Symbol: d . It can be calculated by the formula:

$$d_i = x_i - \bar{x}$$

***3.6 Range.** The difference between the largest and the smallest observed value. Symbol: R_r .

Comment: This quantity is especially useful for small data sets ($n < 10$), as an alternative measure of dispersion. Its principal use is in connection with control charts.

3.7 Standard Deviation. Estimated as the positive square root of the quantity obtained by dividing the sum of squares of deviations between the individual data and the mean of the series by the degrees of freedom (equalling one less than the number of observations for simple replication). Symbol: s (estimated standard deviation) or σ (population standard deviation). It can be calculated by one of the following formulae:

$$s = \sqrt{\frac{\sum d_i^2}{n - 1}} = \sqrt{\frac{\sum x_i^2 - \frac{(\sum x_i)^2}{n}}{n - 1}}$$

Comment: The term "standard error" is often used to indicate the standard deviation of the mean. The minimum number of observations necessary to obtain a useful estimate

of the standard deviation is about six. (For very few degrees of freedom s is quite imprecise and also gives a significantly biased estimate of σ , though Student's t still yields valid confidence intervals.) [W. J. Dixon and F. J. Massey, Introduction to Statistical Analysis, Sect. 9-5, 3rd edition, 1969, McGraw-Hill, New York] The symbol σ is reserved for the population standard deviation.

3.7.1 Standard Deviation from Paired Data. It is possible to estimate standard deviations from larger sets of duplicate measurements made on similar (but not necessarily identical) samples. If m samples are analyzed with the results x_i' and x_i'' , (pertaining to the i th paired measurements), the standard deviation can be calculated by the formula:

$$s = \sqrt{\frac{\sum(x_i' - x_i'')^2}{2m}}$$

with $\nu = m$ degrees of freedom. A text on statistics should be consulted regarding conditions for pairing.

3.7.2 Standard Deviation from Grouped Data. If several sets of analyses are performed (e.g., at different times or on slightly different samples), results may be collected into groups as follows:

1st Group	2nd Group	i-th Group	m-th Group
x_{11}	x_{21}	x_{i1}	x_{m1}
x_{12}	x_{22}	x_{i2}	x_{m2}
x_{13}	x_{23}	x_{i3}	x_{m3}
•	•	•	•
•	•	•	•
•	•	•	•
x_{1j}	x_{2j}	x_{ij}	x_{mj}
•	•	•	•
•	•	•	•
x_{1n_1}	x_{2n_2}	x_{in_i}	x_{mn_m}

numbers of variates in each group:

$$n_1 \qquad n_2 \qquad n_i \qquad n_m$$

arithmetic means in each group:

$$\bar{x}_1 \qquad \bar{x}_2 \qquad \bar{x}_i \qquad \bar{x}_m$$

total number of groups: m

$$\text{total number of data: } n = \sum_1^m n_i$$

The overall standard deviation can be calculated with one of the following equations:

$$s = \sqrt{\frac{\sum_1^m n_i \sum_1^{n_i} (\bar{x}_i - x_{ij})^2}{n - m}} = \sqrt{\frac{\sum_1^m n_i x_{ij}^2 - m \left(\frac{1}{n_i}\right) \left(\sum_1^{n_i} x_{ij}\right)^2}{n - m}}$$

Comment: This quantity is known as the pooled standard deviation. It is equivalent to the square root of the weighted mean variance, where the numbers of degrees of freedom of each of the groups constitute the weights. Its validity rests upon the assumption of homogeneous variance for all groups.

3.8 Variance. The square of the standard deviation. Symbol: V or σ^2 .

3.9 Relative Standard Deviation. The standard deviation divided by the mean of the series. Symbol: s_r (or σ_r). It can be calculated with the formula:

$$s_r = \frac{s}{x}$$

3.10 Percentage Standard Deviation. The value of the relative standard deviation, expressed in percent. Symbol: $s_r(\%)$ [or $\sigma_r(\%)$]. It can be calculated from the relative standard deviation by multiplying by 100.

Comment: It is recommended that the "relative standard deviation" be reported, rather than the "percentage standard deviation," in order to avoid confusion where results themselves are expressed as percentages. The term "coefficient of variation" in place of "relative standard deviation" is not recommended.

*3.11 Error of Result. The value of the result minus the true value (signed quantity). Symbol: e . It can be expressed as:

$$e_i = x_i - \tau$$

Comment: When a result, such as an analyte concentration, is expressed as a percentage, this term will, of course, appear as a percentage. In these circumstances, in order to differentiate between this term and "percentage relative error" (cf. 3.13), it is then permissible to call it "percent absolute error."

3.12 Relative Error. The error divided by the true value. Symbol: e_r . It can be expressed as:

$$e_r = \frac{e}{\tau}$$

3.13 Percentage Relative Error. The relative error expressed in percent. Symbol: $e_r(\%)$. It can be calculated from the relative error by multiplying by 100.

Comment: The term "percentage relative error" should always be quoted in full, rather than "error" or "percentage error," to avoid confusion (cf. the comments to 3.11).

*3.14 Bias. The difference between the population mean and the true value, paying regard to sign. Symbol: Δ . It can be expressed as:

$$\Delta = \mu - \tau$$

Comment: Bias is the total systematic error.

3.15 Confidence Limits about the Mean. Symmetric confidence limits ($\pm C$) about the estimated mean, which cover the population mean with probability $1-\alpha$. The quantity C is calculated by the formula:

$$C = \frac{t_{p,\nu} s}{\sqrt{n}}$$

Here $t_{p,\nu}$ is the critical value from the t - (or Student) distribution function corresponding to the confidence level $1-\alpha$ and degrees of freedom ν . The symbol p represents the percentile (or percentage

point) of the t -distribution. For 1-sided intervals, $p = 1-\alpha$; for 2-sided intervals, $p = 1-\alpha/2$. In each case, the confidence level is $1-\alpha$. Values of t are tabulated in the Appendix (5). The Confidence Interval is given as $\bar{x} \pm C$.

Comment: If the population standard deviation σ is known, confidence limits about a single result may be calculated with the formula:

$$C = t_{p,\infty} \sigma$$

The coefficient $t_{p,\infty}$ is the limiting value of the t -distribution function for $\nu = \infty$ at confidence level $1-\alpha$ [see the last row in the table in the Appendix (5)]. This is identical to z_p , the p -th percentage point of the standard normal variate.

3.16 Geometric (Logarithmic) Mean. The n -th root of the product of the absolute values of the observations, taken with the proper sign. Symbol: \bar{x}_g .

It can be calculated with the formula:

$$\bar{x}_g = \sqrt[n]{(\prod |x_i|)}$$

The Π product is taken from $i = 1$ to n .

Comment: This quantity is often calculated directly from experimental measurements (e.g., determination of concentrations by electrode potential measurements, or pH), although its significance may not always have been recognized. The problem is that the average value of a variable (such as pH) that is a *function* of concentration is not the same as the value of the function at the average concentration. In the case of electrode potentials, the average potential is equivalent to the geometric mean concentration. The correct procedure is to transform to units of concentration before averaging. There is one notable case where the geometric mean is appropriate, namely, when the analyte itself is distributed in a log-normal fashion, as in certain environmental and geological samples.

3.17 Harmonic Mean. The number of observations, divided by the sum of reciprocals of the observations. Symbol: \bar{x}_h . It can be calculated with the formula:

$$\bar{x}_h = \frac{n}{\sum x_j^{-1}}$$

Comment: As in the case of the geometric mean, this quantity is sometimes directly (but inappropriately) calculated, for example, when evaluating kinetic analytical results where the reaction time is inversely proportional to concentration.

3.18 Quadratic Mean. The square root of the expression, in which the sum of squared observations is divided by the number n . Symbol: \bar{x}_q . It can be calculated by the formula:

$$\bar{x}_q = \sqrt{\frac{\sum x_i^2}{n}}$$

Comment: This quantity is also sometimes directly (but inappropriately) calculated, for example, when an observable is proportional to the square of concentration. The quadratic mean, also known as the root mean square, is sometimes appropriate, however, as in certain of the formulae connected with linear calibration functions. (See, for example, sections 4.8 and 4.11.)

3.19 Median. Depending on whether the number of observations is even or odd, the median can be estimated as follows:

- (a): If $n = 2m + 1$: The middle value of a series of observations, arranged in increasing or decreasing order.
- (b): If $n = 2m$: The arithmetic mean of the two middle values of a series of observations, arranged in increasing or decreasing order.

Comment: The use of the median when reporting results of chemical analysis is generally not recommended, because its statistical efficiency is less than that of the mean. In certain cases, however, especially when treating small sets of data, the median may offer advantages because it is a so-called "robust statistic": i.e., it offers considerable resistance to the effects of isolated outliers.

3.20 Mode. The value of the variable occurring with the greatest frequency in the series of observations.

Comment: The use of mode when reporting results of chemical analysis is generally not recommended.

4. QUANTITIES RELATED TO THE USE OF LINEAR CALIBRATION FUNCTIONS

When reporting results obtained from linear calibration functions, the following quantities should also be reported: number of observations (4.1), the equation representing the functional relation (4.5), the standard deviation of observations about the line (4.9), and the estimated (fitted) parameters and their standard deviations. The result of chemical analysis should be quoted as the estimated value of the independent variable (4.14) with its confidence limits (4.15).

4.1 Number of Observations. The total number of points measured when obtaining the calibration function. Symbol: m .

4.2 Degrees of Freedom. The number of observations minus the number of fitted parameters. Symbol: ν . For linear calibration curves $\nu = m - 2$. (See also 3.2.)

4.3 Independent Variable. The quantity (measured or computed), chosen arbitrarily or by design when performing the calibration process. Symbol: x (an individual value represented here as x_j). It is supposed that this value carries no error.

4.4 Dependent Variable. The quantity measured or computed, and plotted as the function of the independent variable. Symbol: y (an individual value represented here as y_j). It is subject to errors and deviations. When performing an analysis, this quantity is measured or computed from the measured signal.

4.5 Equation for the Functional (Calibration) Relation. The equation expressing the linear relation between the dependent and independent variables. This takes the form:

$$y = a + bx$$

where a is the intercept with the y axis and b the slope of the line, both calculated by the method of least squares.

4.6 Slope. This is the parameter b in the calibration equation. It can be calculated by the formula:

$$\hat{b} = \frac{m\sum x_j y_j - \sum x_j \sum y_j}{m\sum x_j^2 - (\sum x_j)^2}$$

4.7 Intercept. This is the parameter a in the calibration equation. It can be calculated by the formula:

$$\hat{a} = \frac{\sum y_j \sum x_j^2 - \sum x_j \sum x_j y_j}{m \sum x_j^2 - (\sum x_j)^2} = (\sum y_j - b \sum x_j) / m$$

4.8 Correlation Coefficient. The terms regression and correlation refer to statistical, as opposed to functional relations among variables. Thus, the statistical parameter estimates for the slope and intercept of the calibration function may be properly described by a correlation coefficient. This is given by:

$$r(a,b) = -\bar{x}/\bar{x}_q$$

Knowledge of this correlation coefficient, and the related confidence ellipse for *mutually* consistent values of a and b , is necessary in certain circumstances. For example, this confidence ellipse may be used to derive bounds for the entire calibration line, i.e., bounds suitable for use with all future values of x . It is important also in two other situations: (a) generating a reduced confidence region for the line, when a or b is known to be restricted to a limited range, and (b) when confidence intervals for *functions* of the estimated parameters (a , b) are desired.

Comment: The rather popular usage of a correlation coefficient as a measure of the co-variation of the dependent variable (y) and the independent variable (x) is not recommended for calibration curves or other functional relations, because r is properly a measure of *statistical* associations.

4.9 Standard Deviation of Points About the Fitted Line. An estimate of the precision of the (dependent variable) measurements. Also known as the residual standard deviation. Symbol: s or s_y . It can be calculated by the formula:

$$s_y = \sqrt{\frac{\sum y_j^2 - \frac{(\sum y_j)^2}{m} - \frac{\left(\sum x_j y_j - \frac{\sum x_j \sum y_j}{m}\right)^2}{\left(\sum x_j^2 - \frac{(\sum x_j)^2}{m}\right)}}{m - 2}}$$

or, more simply from its definition (following the estimation of a and b),

$$s_y = \sqrt{\sum [y - (\hat{a} + \hat{b}x)]^2 / (m - 2)}$$

where $m - 2$ represents the number of degrees of freedom.

4.10 Standard Deviation of the Slope. A quantity related to the precision of the estimated slope of the fitted line. Symbol: s_b . It can be calculated by the formula:

$$s_b = \sqrt{\frac{ms_y^2}{m \sum x_j^2 - (\sum x_j)^2}}$$

4.11 Standard Deviation of the Intercept. A quantity related to the precision of the estimated intercept of the fitted line. Symbol: s_a . It can be calculated by the formula:

$$s_a = s_b \sqrt{\frac{\sum x_j^2}{m}} = s_b \bar{x}_q$$

4.12 Confidence Limits About the Slope. Limits ($\pm C_b$) about the value of slope, corresponding to confidence level $1-\alpha$. The quantity C_b can be calculated by the formula:

$$C_b = t_{p,v} s_b$$

For the meaning of $t_{p,v}$, see 3.15.

4.13 Confidence Limits About the Intercept. Limits ($\pm C_a$) about the value of intercept corresponding to confidence level $1-\alpha$. The quantity C_a can be calculated by the formula:

$$C_a = t_{p,v} s_a$$

For the meaning of $t_{p,v}$, see 3.15. See 4.8 comment concerning the confidence ellipse.

4.14 Estimated Value of the Independent Variable. The value of the independent variable, obtained from a measured or selected value of the dependent variable, y^* through the fitted equation. Symbol: \hat{x} . It can be calculated by the formula:

$$\hat{x} = \frac{y^* - \hat{a}}{\hat{b}}$$

4.15 Confidence Limits About the Fitted Value of the Independent Variable. Limits ($\pm C_x$) about the fitted value of the independent variable, \hat{x} , corresponding to confidence level $1-\alpha$. The quantity C_x can be calculated by the formula:

$$C_x \approx t_{p,v} \frac{s_y}{b} \sqrt{1 + \frac{1}{m} + \frac{m \left[y^* - \frac{\sum y_j}{m} \right]^2}{[m \sum x_j^2 - (\sum x_j)^2] b^2}}$$

For the meaning of $t_{p,v}$, see 3.15. The relation is approximate, because random error in \hat{b} introduces some asymmetry (which can be taken into account with a more rigorous expression). Unless the relative standard deviation of b is large, the approximation is quite adequate (Natrella, 1963, Section 5-4.1).

Comment: If the value \bar{y}^* is obtained as the arithmetic mean of n replicate measurements, the following equation must be used:

$$C_x \approx t_{p,v} \frac{s_y}{b} \sqrt{\frac{1}{n} + \frac{1}{m} + \frac{m \left[\bar{y}^* - \frac{\sum y_j}{m} \right]^2}{[m \sum x_j^2 - (\sum x_j)^2] b^2}}$$

4.16 Estimated Value of the Dependent Variable. The predicted value of the dependent variable which corresponds to a selected value of the independent variable x^* . Symbol: \hat{y} . It can be calculated by the formula:

$$\hat{y} = \hat{a} + \hat{b} x^*$$

4.17 Confidence Limits About the Fitted Value of the Dependent Variable. Limits ($\pm C_y$) about the fitted value of the dependent variable, \hat{y} , corresponding to confidence level $1-\alpha$. The quantity C_y can be calculated by the formula:

$$C_y = t_{p,v} s_y \sqrt{\frac{1}{m} + \frac{m \left[x^* - \frac{\sum x_j}{m} \right]^2}{m \sum x_j^2 - (\sum x_j)^2}}$$

For the meaning of $t_{p,v}$, see 3.15.

4.18 Minimum Significant Signal (Critical Level). The minimum value of the net signal, $y - \hat{a}$, that is statistically significant. Symbol: S_C . It can be calculated by the formula:

$$S_C = t_{p,v} s_o$$

where $t_{p,v}$ is the critical value from the t -distribution (3.15), and s_o is the estimated standard deviation of the net signal when $x = 0$:

$$s_o = (s_a^2 + s_y^2)^{1/2}$$

Comment: S_C is employed to make Detection Decisions. If the observed net signal exceeds S_C , it is considered "Detected" at the $(1-p)$ significance level since this is a 1-sided test.

4.19 Minimum Detectable Quantity (Detection Limit). The minimum value of the independent variable that can be confidently detected (probability p), when S_C is employed as the decision threshold. Symbol: x_D . It can be calculated by the formula:

$$x_D = 2(S_C / b)(K/I)$$

where:

$$K = 1 + r(a,b)(s_d/s_o)t_{p,v}(s_y/b)$$

$$I = 1 - t_{p,v}^2 (s_y/b)^2$$

Comment: x_D , as indicated above, is strictly speaking an *estimate* for the minimum detectable quantity; it is the maximum null-signal upper limit for a *particular realization* of the calibration curve. If σ_y were known without error, the relative uncertainty interval of x_D would be no greater than that of the slope. When s_y is used as an estimate of σ_y , the uncertainty in x_D is further amplified by the confidence interval for σ/s . Note that the ratio $K/I \approx 1$ when $s_b \ll b/t_{p,v}$; when $s_b \geq b/t_{p,v}$, the uncertainty in the detection limit is unbounded (Currie, 1984).

5. APPENDIX

Critical values (limits of integration) of the t (or Student) distribution.

Degrees of Freedom (ν)	2-Sided Confidence Level ($1-\alpha$)	0.90	0.95	0.99	0.997
	Percentile (p)	0.95	0.975	0.995	0.9986
1		6.31	12.71	63.66	235
2		2.92	4.30	9.92	19.2
3		2.35	3.18	5.84	9.22
4		2.13	2.78	4.60	6.62
5		2.02	2.57	4.03	5.51
6		1.94	2.45	3.71	4.90
7		1.90	2.37	3.50	4.53
8		1.86	2.31	3.36	4.27
9		1.83	2.26	3.25	4.09
10		1.81	2.23	3.17	3.98
24		1.71	2.06	2.80	3.34
∞		1.64	1.96	2.58	3.00

REFERENCES

In formulating these recommendations the Commission considered the following list of documents pertaining to nomenclature and symbols:

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