

2.3 Quantities related to replicate measurements

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

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*.

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: ***n***. For simple replication, with *n* measurements and one estimated parameter (the mean), ***n*** = *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 2.4).

Confidence Level

The probability of covering the expected value of an estimated parameter with an interval estimate for that parameter. (Symbol *1 - α*). 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 - α* = 0.95 is recommended.

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:

$$\bar{x} = \frac{\sum x_i}{n} \quad (2)$$

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 ***m***. That is, ***m*** is the limiting value for \bar{x} , as ***n*** $\rightarrow \infty$.

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:

$$\bar{x}_w = \frac{\sum w_i x_i}{\sum w_i} \quad (3)$$

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

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:

$$d_i = x_i - \bar{x} \quad (4)$$

Range

The difference between the largest and the smallest observed value. Symbol: R_x .

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.

Standard Deviation

Calculated 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:

$$s = \sqrt{\frac{\sum d_i^2}{n-1}} = \sqrt{\frac{\sum x_i^2 - \frac{(\sum x_i)^2}{n}}{n-1}} \quad (5)$$

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.

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:

$$s = \sqrt{\frac{\sum (x_i' - x_i'')^2}{2m}} \quad (6)$$

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

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 (Table 2.1).

TABLE 2.1

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

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

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

$$s = \sqrt{\frac{\sum_1^m \sum_1^{n_i} (\bar{x}_i - x_{ij})^2}{n - m}} = \sqrt{\frac{\sum_1^m \sum_1^{n_i} x_{ij}^2 - \sum_1^m \left(\frac{1}{n_i}\right) \left(\sum_1^{n_i} x_{ij}\right)^2}{n - m}} \quad (7)$$

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.

Variance

The square of the population standard deviation. Symbol: V or s^2 .

Relative Standard Deviation

The standard deviation divided by the mean of the series. Symbol: s_r (or \mathbf{s}_r). It can be calculated with the formula:

$$s_r = \frac{s}{\bar{x}} \quad (8)$$

Percentage Standard Deviation

The value of the relative standard deviation, expressed in percent. Symbol: $s_r (\%)$ [or $\mathbf{s}_r (\%)$]. 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.

Error of Result

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

$$e_i = x_i - t \quad (9)$$

Comment: When a result, such as an estimated 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*, it is then permissible to call it "percent absolute error."

Relative Error

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

$$e_r = \frac{e}{t} \quad (10)$$

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.

Bias

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

$$\Delta = m - t \quad (11)$$

Comment: Bias is the total systematic error.

Confidence Limits about the Mean

Symmetric confidence limits ($\pm C$) about the estimated mean forming an interval that covers the population mean with probability $1 - \alpha$. The quantity C is calculated by the formula:

$$C = \frac{t_{p,n} s}{\sqrt{n}} \quad (12)$$

Here $t_{p,v}$ is the critical value from the t - (or Student) distribution function corresponding to the confidence level $1 - \alpha$ and degrees of freedom n . 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 (2.5). The *confidence interval* is given as $\bar{x} \pm C$.

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

$$C = t_{p,\infty} s \quad (13)$$

The coefficient $t_{p,\infty}$ is the limiting value of the t -distribution function for $n = \infty$ at confidence level $1 - \alpha$ [see the last row in the table in the Appendix (2.5)]. This is identical to z_p , the p -th percentage point of the standard normal variate.

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:

$$\bar{x}_g = \sqrt[n]{\left(\prod |x_i|\right)} \quad (14)$$

The \prod 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.

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:

$$\bar{x}_h = \frac{n}{\sum x_j^{-1}} \quad (15)$$

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.

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:

$$\bar{x}_q = \sqrt{\frac{\sum x_i^2}{n}} \quad (16)$$

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, *Correlation Coefficient* and *Standard Deviation of the Intercept* in Section 2.4).

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.

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.