Appendix I Propagation of Uncertainties in Physical Measurements
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e made with an vity that is not , small variations among replicate measurements are observed. These variations represent the accumulation of a large number of random extraneous signals (noise) that develop in various instrument components. In some instances, the direction of the noise from most of the components will, by chance, be positive, and a higher than average reading will result; at other times, negative noise signals may predominate, leading to a result that is less than average. The most probable event, however, is for the number and size of the negative and positive noise signals to be about the same, thus giving a reading that approaches an average or mean value.

For a large number of replicate measurements, the accumulated uncertainties due to random noise cause the results to be distributed in the symmetrical way shown in Figure A-1. This distribution, which is termed *Gaussian*, can be described in terms of three parameters; that is,

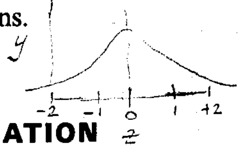
$$y = \frac{e^{-(x_i-\mu)^2/2\sigma^2}}{\sigma\sqrt{2\pi}} = \frac{e^{-z^2/2}}{\sigma\sqrt{2\pi}} \qquad \text{(A-1)}$$

In this equation, x_i represents values of individual measurements, and μ is the arithmetic mean for an infinite number of such measurements. The quantity $(x_i - \mu)$ is thus the deviation from the mean; y is the frequency of occurrence for each value of $(x_i - \mu)$. The symbol π has its usual meaning, and e is the base for Napierian logarithms. The parameter σ is called the *standard deviation* and is a constant that has a unique value for any set of data comprising a large number of measurements. The breadth of the normal error curve, which increases as the precision of a measurement decreases, is directly related to σ. Thus, σ is widely employed to define the precision of instruments.

The exponential term in Equation A-1 can be simplified by introducing the variable

$$z = \frac{x_i - \mu}{\sigma} \qquad \text{(A-2)}$$

which then gives the deviation from the mean in units of standard deviations.



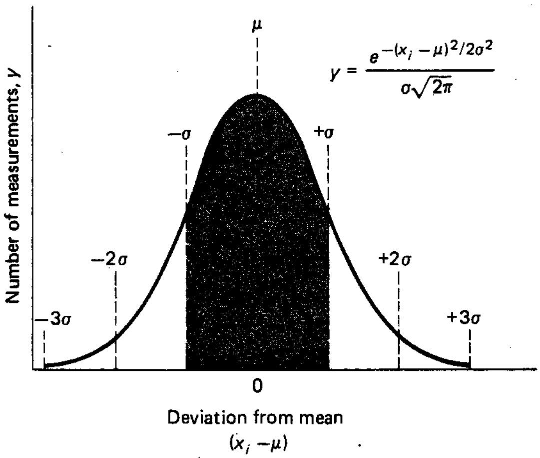


FIGURE A-1 A normal or Gaussian distribution curve.

THE STANDARD DEVIATION

Equation A-1 indicates that a unique distribution curve exists for each value of the standard deviation. Regardless of the size of σ, however, it can be shown that 68.3% of the area beneath the curve lies within one standard deviation ($\pm 1\sigma$) of the mean, μ (shaded region, Figure A-1). Thus, 68.3% of the results from replicated measurements would be expected to lie within these boundaries. Approximately 95.5% of all values should lie within $\pm 2\sigma$; 99.7% should appear within $\pm 3\sigma$. Values of $(x_i - \mu)$ corresponding to $\pm 1\sigma$, $\pm 2\sigma$, and $\pm 3\sigma$ are indicated by broken vertical lines in Figure A-1.

These properties of a Gaussian curve are useful because they permit statements to be made about the probable magnitude of the uncertainty for any given measurement, *provided the standard deviation for the output of an instrument is known.* Thus, if σ for an instrument is available, one can say that the chances are 68.3 out of 100 that the uncertainty associated with any *single* measurement is smaller than $\pm 1\sigma$, that the chances are 95.5 out of 100 that the error is less than $\pm 2\sigma$, and so forth. Clearly, the standard deviation for a method of measurement is a useful quantity for estimating and reporting the probable size of instrumental uncertainties arising from random noise.

For a very large set of data the standard deviation is given by

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \mu)^2}{N}} \qquad \text{(A-3)}$$

Here, the sum of the squares of the individual deviations from the mean $(x_i - \mu)$ is divided by the total number of measurements in the set, N. Extraction of the square root of this quotient gives σ.

Equations A-1 and A-3 apply exactly only as the number of measurements approaches infinity. When N is small, a better estimate for the standard deviation is given by

$$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}} \qquad \text{(A-4)}$$

\# of degrees of freedom

Note that the symbol s is used to distinguish the experimentally realizable estimate of the standard deviation from the theoretical σ. Furthermore, the experimental mean of this set $\bar{x}$ can only approximate the true mean for an infinite number of measurements μ. When N is greater than 20 to 30, it is usually safe to assume that $s \rightarrow \sigma$.

EXAMPLE

The following data were obtained for the determination of mercury in the flesh of a trout by a fluorescence method: 1.67, 1.63, and 1.70 ppm. Calculate the standard deviation for the measurement.

x_i	$x_i - \bar{x}$	$(x_i - \bar{x})^2$
1.67	0.003	0.00001
1.63	−0.037	0.00137
1.70	0.033	0.00109
$3 \lvert 5.00$		$\sum_{i=1}^{3} (x_i - \bar{x})^2 = 0.00247$
$x = 1.667$		

$$s = \sqrt{\frac{0.00247}{3 - 1}} = 0.351 = 0.04$$

Generally, in a calculation of this type, it is wise to avoid rounding until the final result has been obtained.

Another precision term widely employed by statisticians is the *variance*, which is equal to σ^2. Most experimental scientists prefer to employ σ rather than σ^2 because the units of the standard deviation are the same as those of the quantity measured.

CONFIDENCE INTERVALS

The true mean value (μ) of a measurement is a constant that must always remain unknown. With the aid of statistical theory, however, limits may be set about the experimentally determined mean $(\bar{x})$ within which we may expect to find the true mean with a given degree of probability; the limits obtained in this manner are called *confidence limits*. The interval defined by these limits is known as the *confidence interval*. The confidence interval can be determined from the value of z in Equation A-2. For example, if z is given a value of $+1$, then Equation A-2 takes the form

$$x_i - \mu = \sigma$$

and if z is equal to -1,

$$x_i - \mu = -\sigma$$

As mentioned earlier, approximately 68% of the area under a normal distribution curve lies within the limits of $\pm 1\sigma$. Thus, there exists a 68% probability that the deviation from the mean $(x_i - \mu)$ for any *single* measurement will be within this interval. Similarly, when z is equal to ± 2,

$$x_i - \mu = \pm 2\sigma$$

Here, 96% of the area under the curve lies within these limits; thus there exists a 96% probability that the deviation from the mean of an individual measurement will lie within this range. Areas in terms of percentages are termed *confidence levels*. Confidence levels for a few values of z are given below.

Calculated from a normal distribution curve

$CL = \int_{-z}^{+z} y$

Confidence Level	50%	68%	90%
z	± 0.67	± 1.00	± 1.64
Confidence Level	95%	96%	99%
z	± 1.96	± 2.00	± 2.58

The confidence limit for a single measurement is obtained by rearranging Equation A-2 to

$$\text{confidence limit for } \mu = x_i - z\sigma$$

When x_i is replaced by $\bar{x}$, the mean for several measurements, the confidence limit is decreased by $\sqrt{N}$. Thus, a more general expression is

$$\text{confidence limit for } \mu = \bar{x} - \frac{z\sigma}{\sqrt{N}} \quad \text{(A-5)}$$

The example that follows illustrates the calculation of confidence limits.

EXAMPLE

From 25 replicate measurements, the standard deviation for the fluorescence method used in the earlier example was found to be 0.07 ppm Hg. Calculate the 50 and 95% confidence limits for the mean of the three analyses.

For the 50% confidence level, $z = \pm 0.67$, and

$$50\% \text{ confidence limit} = 1.67 \pm \frac{0.67 \times 0.07}{\sqrt{3}}$$
$$= 1.67 \pm 0.03$$

Similarly,

$$95\% \text{ confidence limit} = 1.67 \pm \frac{1.96 \times 0.07}{\sqrt{3}}$$
$$= 1.67 \pm 0.08$$

Thus, the chances are 50 in 100 that the true mean μ will lie in the interval between 1.64 and 1.70 ppm Hg; there is a 95% chance that the true mean lies between 1.59 and 1.75 ppm.

It should be noted that the standard deviation from the three measurements themselves was *not* employed in calculating the confidence limit in the foregoing example. With such a small number of measurements, there is no assurance that $s \to \sigma$; indeed, s for the three data in question is considerably smaller (0.04) than the value of 0.07 that was obtained from 25 replicate measurements. Without this sure knowledge of the standard deviation, the confidence limit would have had to be widened.[1]

PROPAGATION OF UNCERTAINTIES IN A CALCULATED RESULT

The result of an analysis is typically calculated from two or more experimental data, each of which has associated with it an uncertainty due to random noise. It is worthwhile exploring the ways in which these various uncertainties accumulate in the final result. For

[1] For methods of treating data when σ is not known, see D. A. Skoog and D. M. West, *Fundamentals of Analytical Chemistry*, 3d ed. New York: Holt, Rinehart and Winston, 1976, p. 64.

Also in Che Handbook

the purpose of such an analysis, let us assume that the measured quantity x is dependent upon the variables $p, q, r, \ldots$, which fluctuate in a random and independent manner. That is, x is a function f of $p, q, r, \ldots$, so that we may write

$$x = f(p, q, r, \ldots) \tag{A-6}$$

The uncertainty dx_i (that is, the deviation from the mean) in the ith measurement of x will depend upon the size and signs of the corresponding uncertainties $dp_i, dq_i, dr_i, \ldots$. That is,

$$dx_i = f(dp_i, dq_i, dr_i, \ldots) = (x_i - \mu)$$

The variation in dx as a function of the uncertainties in $p, q, r, \ldots$, can be derived by taking the total differential of Equation A-6. That is,

$$dx = \left(\frac{\delta x}{\delta p}\right)_{q,r,\ldots} dp + \left(\frac{\delta x}{\delta q}\right)_{p,r,\ldots} dq + \left(\frac{\delta x}{\delta r}\right)_{p,q,\ldots} dr + \cdots \tag{A-7}$$

In order to relate the various terms in Equation A-7 to the standard deviation of x, p, q, and r as given by Equation A-3, it is necessary to square the foregoing equation. Thus,

$$(dx)^2 = \left[\left(\frac{\delta x}{\delta p}\right)_{q,r,\ldots} dp + \left(\frac{\delta x}{\delta q}\right)_{p,r,\ldots} dq + \left(\frac{\delta x}{\delta r}\right)_{p,q,\ldots} dr + \cdots\right]^2 \tag{A-8}$$

Then, the resulting equation must be summed between the limits of $i = 1$ to $i = N$, where N again is the total number of replicate measurements (Equation A-3). $\sum_{i=1}^{i=N} (dx)^2 = \sum (x_i - \mu)^2$

In squaring Equation A-7, two types of terms from the right-hand side of the equation become evident. The first are type 1 terms, such as

$$\left[\left(\frac{\delta x}{\delta p}\right) dp\right]^2, \left[\left(\frac{\delta x}{\delta q}\right) dq\right]^2, \left[\left(\frac{\delta x}{\delta r}\right) dr\right]^2$$

Because they are squares, type 1 terms *will always be positive. Therefore, these terms can never cancel.* In contrast, type 2 terms (called *cross terms*) may be either positive or negative in sign. Examples of these terms are

$$\left(\frac{\delta x}{\delta p}\right)\left(\frac{\delta x}{\delta q}\right) dpdq, \left(\frac{\delta x}{\delta p}\right)\left(\frac{\delta x}{\delta r}\right) dpdr$$

If dp, dq, and dr are independent and random, some of the cross terms will be negative and others positive. Thus, the *summation of all such terms should approach zero.*

As a consequence of the canceling tendency of type 2 terms, the square of Equation A-8 can be readily obtained and summed from $i = 1$ to N. Thus,

$$\sum_{i=1}^{N} (dx_i)^2 = \left(\frac{\delta x}{\delta p}\right)^2 \sum_{i=1}^{N} (dp_i)^2 + \left(\frac{\delta x}{\delta q}\right)^2 \sum_{i=1}^{N} (dq_i)^2 + \left(\frac{\delta x}{\delta r}\right)^2 \sum_{i=1}^{N} (dr_i)^2 + \cdots$$

Dividing through by N gives

$$\frac{\sum (dx_i)^2}{N} = \left(\frac{\delta x}{\delta p}\right)^2 \frac{\sum (dp_i)^2}{N} + \left(\frac{\delta x}{\delta q}\right)^2 \frac{\sum (dq_i)^2}{N} + \left(\frac{\delta x}{\delta r}\right)^2 \frac{\sum (dr_i)^2}{N} + \cdots \tag{A-9}$$

From Equation A-3, however, we see that

$$\frac{\sum (dx_i)^2}{N} = \frac{\sum (x_i - \mu)^2}{N} = \sigma_x^2$$

where σ_x^2 is the variance of x. Similarly,

$$\frac{\sum (dp_i)^2}{N} = \sigma_p^2$$

and so forth. Thus, Equation A-9 can be written in terms of the variances of the quantities; that is,

$$\sigma_x^2 = \left(\frac{\delta x}{\delta p}\right)^2 \sigma_p^2 + \left(\frac{\delta x}{\delta q}\right)^2 \sigma_q^2 + \left(\frac{\delta x}{\delta r}\right)^2 \sigma_r^2 + \cdots \tag{A-10}$$

The example that follows demonstrates an application of Equation A-10.

EXAMPLE

The chloride in a 0.1200-g (± 0.0002) sample was determined by coulometric titration with silver ions (p. 597). An end point was reached after 167.4 (± 0.3) s with a current of 20.00 mA (± 0.04). Titration of a blank required 13.2 (± 0.3) s with the same current. The numbers in parentheses are absolute standard deviations associated with each measurement. What is the relative and absolute standard deviation for the percent chloride?

$\Delta T_s = 167.4 (\pm.3)s$
$\Delta T_{blank} = 13.2 (\pm.3)s$

The percent chloride is given by

$I = 20.00 \text{ mA} (\pm.04)$
$W = 0.1200 \text{ g} (\pm.0002)$

$$x = \% \text{ Cl} = \frac{k(T - T_0)I}{W} \tag{A-11}$$

where T and T_0 are the times (in seconds) for titration of the sample and blank, respectively, I is the current in mA, W is the sample weight in g, and k is a constant whose value (3.6742×10^{-5}) is known with a high degree of precision.

To employ Equation A-10, we first take the partial derivative of percent chloride with respect to T, holding the other variables constant. Thus,

$$\left(\frac{\delta x}{\delta T}\right)_{T_0, I, W} = \frac{kI}{W}$$

Similarly,

$$\left(\frac{\delta x}{\delta T_0}\right)_{T, I, W} = -\frac{kI}{W}$$

and

$$\left(\frac{\delta x}{\delta I}\right)_{T, T_0, W} = \frac{k(T - T_0)}{W}$$

Finally,

$$\left(\frac{\delta x}{\delta W}\right)_{T, T_0, I} = -\frac{k(T - T_0)I}{W^2}$$

Applying Equation A-10 gives

$$\sigma_x^2 = \left(\frac{kI}{W}\right)^2 \sigma_T^2 + \left(-\frac{kI}{W}\right)^2 \sigma_{T_0}^2 + \left[\frac{k(T - T_0)}{W}\right]^2 \sigma_I^2 + \left[-\frac{k(T - T_0)I}{W^2}\right]^2 \sigma_W^2$$

Dividing this equation by the square of Equation A-11 gives

$$\left(\frac{\sigma_x}{x}\right)^2 = \left(\frac{\sigma_T}{T - T_0}\right)^2 + \left(-\frac{\sigma_{T_0}}{T - T_0}\right)^2 + \left(\frac{\sigma_I}{I}\right)^2 + \left(-\frac{\sigma_W}{W}\right)^2$$

or

$$\left(\frac{\sigma_x}{x}\right)^2 = \frac{(\sigma_T)^2 + (-\sigma_{T_0})^2}{(T - T_0)^2} + \left(\frac{\sigma_I}{I}\right)^2 + \left(-\frac{\sigma_W}{W}\right)^2 \tag{A-12}$$

Substitution of the numerical data into Equation A-11 gives

$$x = \% \text{ Cl} = \frac{3.6742 \times 10^{-5}(167.4 - 13.2) \times 20.00}{0.1200} = 0.94427$$

Substitution of numerical values into Equation A-12 yields

$$\left(\frac{\sigma_x}{x}\right)^2 = \frac{(0.3)^2 + (-0.3)^2}{(167.4 - 13.2)^2} + \left(\frac{0.04}{20.00}\right)^2 + \left(-\frac{0.0002}{0.1200}\right)^2$$
$$= 7.57 \times 10^{-6} + 4.00 \times 10^{-6} + 2.78 \times 10^{-6}$$

$$\frac{\sigma_x}{x} = \sqrt{1.435 \times 10^{-5}} = 3.8 \times 10^{-3}$$

Thus, the relative standard deviation for the analysis would be expected to be about 4 ppt. To obtain the absolute standard deviation, we write

$$\sigma_x = 0.9943 \times 3.8 \times 10^{-3} = 0.0038\% \text{ Cl}$$

and the result could be reported as

$$\% \text{ Cl} = 0.994(\pm 0.004)$$

The foregoing example illustrates two important, general statistical relationships.

(1) The *absolute* variance of a sum or difference is the sum of the individual *absolute* variances.

(2) The *relative* variance of a product or quotient is the sum of the individual *relative* variances. Thus, for the relation $y = a + b$ or $y = a - b$,

$$\sigma_y^2 = \sigma_a^2 + \sigma_b^2$$

and the standard deviation of y is

$$\sigma_y = \sqrt{\sigma_a^2 + \sigma_b^2}$$

In contrast, when $y = a \cdot b$ or $y = a/b$,

$$\left(\frac{\sigma_y}{y}\right)^2 = \left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2$$

or

$$\frac{\sigma_y}{y} = \sqrt{\left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2}$$

Note in the example that it was first necessary to add the absolute variances of T and T_0 to give the absolute variance of the difference between the two numbers. After this the *relative* variance was calculated. It was then combined with the *relative* variances of the other two numbers (I and W) making up the quotient to give the *relative* variance of the quotient.

Propagation of error :

error of volumetric flask
0.5L

error on Eppendorf (from manual)
0.120 mL = 120 μL
(yellow) for ~100μL error 1.0%

$$C_{final} = \frac{(C_{ini})\, V_1}{V_2}$$

$$\left(\frac{\sigma_{c_f}}{c_f}\right)^2 = \left(\frac{\sigma_{c_{ini}}}{C_{ini}}\right)^2 + \left(\frac{\sigma_{V_1}}{V_1}\right)^2 + \left(-\frac{\sigma_{V_2}}{V_2}\right)^2$$

$\sigma_{c_{ini}}$ = from std dev 0.03 g/L ✓

σ_{V_i} = 1% of 120 μL

σ_{V_2} = ±0.20 mL for 500mL vol flask

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$$\left(\frac{\sigma}{c_f}\right)^2 = \left(\frac{0.03\ g/L}{409.87\ g/L}\right)^2 + \left(\frac{1.2\,\mu L}{120\,\mu L}\right)^2 + \left(\frac{0.20\ mL}{500\ mL}\right)^2$$

$$\left(\frac{\sigma}{c_f}\right) = \sqrt{5.36\times10^{-9} + 1\times10^{-4} + 1.6\times10^{-7}}$$

dominating term !

$$\left(\frac{\sigma}{c_f}\right) = 0.01$$

e.g. 1% error on new sample