Sometimes a Type B evaluation of uncertainty involves making a best guess based on all available information and professional judgment. Laboratory workers may be reluctant to make this kind of evaluation, but it is better to make an informed guess about an uncertainty component than to ignore it completely.

A standard uncertainty $u(x_i)$ may be called a "Type A" or "Type B" standard uncertainty, depending on its method of evaluation, but no distinction is made between the two types for the purposes of uncertainty propagation.

19.3.4 Corrections for Systematic Effects

When a systematic effect in the measurement process has been identified and quantified, a quantity should be included in the mathematical measurement model to correct for it. The quantity, called a *correction* (additive) or *correction factor* (multiplicative), will have an uncertainty which should be evaluated and propagated.

Whenever a previously unrecognized systematic effect is detected, the effect should be investigated and either eliminated procedurally or corrected mathematically.

19.3.5 Counting Uncertainty

The *counting uncertainty* of a radiation measurement (historically called "counting error") is the component of uncertainty caused by the random nature of radioactive decay and radiation counting. Radioactive decay is inherently random in the sense that two atoms of a radionuclide will generally decay at different times, even if they are identical in every discernible way. Radiation counting is also inherently random unless the efficiency of the counting instrument is 100 %.

In many cases the counting uncertainty in a single gross radiation counting measurement can be estimated by the square root of the observed counts. The Poisson model of radiation counting, which is the mathematical basis for this rule, is discussed in Section 19.5. Note that the use of this approximation is a Type B evaluation of uncertainty.

Historically many radiochemistry laboratories reported only the counting uncertainties of their measured results. MARLAP recommends that a laboratory consider all possible sources of measurement uncertainty and evaluate and propagate the uncertainties from all sources believed to be potentially significant in the final result.

19.3.6 Expanded Uncertainty

When a laboratory reports the result of a measurement, it may report the combined standard uncertainty, $u_c(y)$, or it may multiply $u_c(y)$ by a factor k, called a *coverage factor*, to produce an *expanded uncertainty*, denoted by U, such that the interval from $y - U$ to $y + U$ has a specified

high probability p of containing the value of the measurand. The specified probability, p, is called the *level of confidence* or the *coverage probability* and is generally only an approximation of the true probability of coverage.

When the distribution of the measured result is approximately normal, the coverage factor is often chosen to be $k = 2$ for a coverage probability of approximately 95 %. An expanded uncertainty calculated with $k = 2$ or 3 is sometimes informally called a "two-sigma" or "three-sigma" uncertainty. In general, if the desired coverage probability is γ and the combined standard uncertainty is believed to be an accurate estimate of the standard deviation of the measurement process, the coverage factor for a normally distributed result is $k = z_{(1+\gamma)/2}$, which can be found in a table of quantiles of the standard normal distribution (see Table G.1 in Appendix G).

The *GUM* recommends the use of coverage factors in the range 2–3 when the combined standard uncertainty represents a good estimate of the true standard deviation. Attachment 19D describes a more general procedure for calculating the coverage factor, k_p, that gives a desired coverage probability p when there is substantial uncertainty in the value of $u_c(y)$.

The *GUM* does not assign a name to the interval $y \pm U$, but it clearly states that the interval should not be called a "confidence interval," because this term has a precise statistical definition and the interval described by the expanded uncertainty usually does not meet the requirements. The interval $y \pm U$ is sometimes called an "uncertainty interval."[5]

19.3.7 Significant Figures

The number of significant figures that should be reported for the result of a measurement depends on the uncertainty of the result. A common convention is to round the uncertainty (standard uncertainty or expanded uncertainty) to either one or two significant figures and to report both the measured value and the uncertainty to the resulting number of decimal places (ISO, 1995; Bevington, 1992; EPA, 1980; ANSI N42.23). MARLAP recommends this convention and suggests that uncertainties be rounded to two figures. The following examples demonstrate the application of the rule.

[5] When the distribution of the result is highly asymmetric, so that the result is more likely to fall on one side of the value of the measurand than the other, the use of a single expanded uncertainty, U, to construct a symmetric uncertainty interval about the result may be misleading, especially if one wishes to state an approximate coverage probability for the interval. However, methods for constructing an asymmetric uncertainty interval with a stated coverage probability are beyond the scope of this chapter and require more information than that provided by the input estimates, their standard uncertainties, and estimated covariances (e.g., Monte Carlo simulation). Note that the value of the combined standard uncertainty is unaffected by the symmetry or asymmetry of the distribution.

EXAMPLES

MEASURED VALUE (y)	EXPANDED UNCERTAINTY $U = k u_c(y)$	REPORTED RESULT
0.8961	0.0234	0.896 ± 0.023
0.8961	0.2342	0.90 ± 0.23
0.8961	2.3419	0.9 ± 2.3
0.8961	23.4194	1 ± 23
0.8961	234.1944	0 ± 230

Only final results should be rounded in this manner. Intermediate results in a series of calculation steps should be carried through all steps with additional figures to prevent unnecessary roundoff errors. Additional figures are also recommended when the data are stored electronically. Rounding should be performed only when the result is reported. (See Section 19.5.11 for a discussion of the measurement uncertainty associated with rounding.)

19.3.8 Reporting the Measurement Uncertainty

When a measured value y is reported, its uncertainty should always be stated. The laboratory may report either the combined standard uncertainty $u_c(y)$ or the expanded uncertainty U.

The measured value, y, and its expanded uncertainty, U, may be reported in the format $y \pm U$ or y +– U.

The plus-minus format may be used to report an expanded uncertainty, but it generally should be avoided when reporting a standard uncertainty, because readers are likely to interpret it as a confidence interval with a high coverage probability. A commonly used shorthand format for reporting a result with its standard uncertainty places the one or two digits of the standard uncertainty in parentheses immediately after the corresponding final digits of the rounded result. For example, if the rounded result of the measurement is 1.92 and the standard uncertainty is 0.14, the result and uncertainty may be shown together as 1.92(14). Another acceptable reporting format places the entire standard uncertainty in parentheses. The result in the preceding example would appear in this format as 1.92(0.14). The laboratory may also report the standard uncertainty explicitly.

Since laboratories may calculate uncertainties using different methods and report them using different coverage factors, it is a bad practice to report an uncertainty without explaining what it represents. Any analytical report, even one consisting of only a table of results, should state

whether the uncertainty is the combined standard uncertainty or an expanded uncertainty, and in the latter case it should also state the coverage factor used and, if possible, the approximate coverage probability. A complete report should also describe the methods used to calculate the uncertainties. If the laboratory uses a shorthand format for the uncertainty, the report should include an explanation of the format.

The uncertainties for environmental radioactivity measurements should be reported in the same units as the results. Relative uncertainties (i.e., uncertainties expressed as percentages) may also be reported, but the reporting of relative uncertainties alone is not recommended when the measured value may be zero, because the relative uncertainty in this case is undefined. A particularly bad practice, sometimes implemented in software, is to compute the relative uncertainty first and multiply it by the measured value to obtain the absolute uncertainty. When the measured value is zero, the uncertainty is reported incorrectly as zero. Reporting of relative uncertainties without absolute uncertainties for measurements of spiked samples or standards generally presents no problems, because the probability of a negative or zero result is negligible.

It is possible to calculate radioanalytical results that are less than zero, although negative radioactivity is physically impossible. Laboratories sometimes choose not to report negative results or results that are near zero. Such censoring of results is *not* recommended. *All results, whether positive, negative, or zero, should be reported as obtained, together with their uncertainties.*

The preceding statement must be qualified, because a measured value y may be so far below zero that it indicates a possible blunder, procedural failure, or other quality control problem. Usually, if $y + 3u_c(y) < 0$, the result should be considered invalid, although the accuracy of the uncertainty estimate $u_c(y)$ must be considered, especially in cases where only few counts are observed during the measurement and counting uncertainty is the dominant component of $u_c(y)$. (See Chapter 18, *Laboratory Quality Control*, and Attachment 19D of this chapter.)

19.3.9 Recommendations

MARLAP makes the following recommendations to radioanalytical laboratories.

- All radioanalytical laboratories should adopt the terminology and methods of the *Guide to the Expression of Uncertainty in Measurement* (ISO, 1995) for evaluating and reporting measurement uncertainty.

- The laboratory should follow QC procedures that ensure the measurement process remains in a state of statistical control, which is a prerequisite for uncertainty evaluation.

- Uncertainty estimates should account for both random and systematic effects in the measurement process, but they should not account for possible blunders or other spurious errors. Spurious errors indicate a loss of statistical control of the process.

- The laboratory should report each measured value with either its combined standard uncertainty or its expanded uncertainty.

- The reported measurement uncertainties should be clearly explained. In particular, when an expanded uncertainty is reported, the coverage factor should be stated, and, if possible, the approximate coverage probability should also be given.

- A laboratory should consider all possible sources of measurement uncertainty and evaluate and propagate the uncertainties from all sources believed to be potentially significant in the final result.

- Each uncertainty should be rounded to either one or two significant figures, and the measured value should be rounded to the same number of decimal places as its uncertainty. (MARLAP prefers the use of two figures in the uncertainty.) Only final results should be rounded in this manner.

- The laboratory should report all results, whether positive, negative, or zero, as obtained, together with their uncertainties.

MARLAP makes no recommendations regarding the presentation of radioanalytical data by the laboratory's clients or other end users of the data.

19.4 Procedures for Evaluating Uncertainty

The usual steps for evaluating and reporting the uncertainty of a measurement may be summarized as follows (adapted from Chapter 8 of the *GUM*):

1. Identify the measurand, Y, and all the input quantities, X_i, for the mathematical model. Include all quantities whose variability or uncertainty could have a potentially significant effect on the result. Express the mathematical relationship, $Y = f(X_1, X_2, \ldots, X_N)$, between the measurand and the input quantities.

2. Determine an estimate, x_i, of the value of each input quantity, X_i (an "input estimate," as defined in Section 19.3.2).

3. Evaluate the standard uncertainty, $u(x_i)$, for each input estimate, x_i, using either a Type A or Type B method of evaluation (see Section 19.3.3).

4. Evaluate the covariances, $u(x_i, x_j)$, for all pairs of input estimates with potentially significant correlations.

5. Calculate the estimate, y, of the measurand from the relationship $y = f(x_1, x_2, \ldots, x_N)$, where f is the function determined in Step 1.

6. Determine the combined standard uncertainty, $u_c(y)$, of the estimate, y (see Section 19.3.3).

7. Optionally multiply $u_c(y)$ by a coverage factor k to obtain the expanded uncertainty U such that the interval $[y - U, y + U]$ can be expected to contain the value of the measurand with a specified probability (see Section 19.3.6 and Attachment 19D).

8. Report the result as $y \pm U$ with the unit of measurement, and, at a minimum, state the coverage factor used to compute U and the estimated coverage probability. Alternatively, report the result, y, and its combined standard uncertainty, $u_c(y)$, with the unit of measurement.

19.4.1 Identifying Sources of Uncertainty

The procedure for assessing the uncertainty of a measurement begins with listing all conceivable sources of uncertainty in the measurement process. Even if a mathematical model has been identified, further thought may lead to the inclusion of more quantities in the model. Some sources of uncertainty will be more significant than others, but all should be listed.

After all conceivable sources of uncertainty are listed, they should be categorized as either potentially significant or negligible. Each uncertainty that is potentially significant should be evaluated quantitatively. The following sources of uncertainty may not always be significant but should at least be considered:

- radiation counting
- instrument calibration (e.g., counting efficiency)
- tracers, carriers, or other methods of yield measurement
- variable instrument backgrounds
- variable counting efficiency (e.g., due to the instrument or to source geometry and placement)
- contamination of reagents and tracers
- interferences, such as crosstalk and spillover
- baseline determination (gamma-ray spectrometry)
- laboratory subsampling

Other sources of uncertainty include:

- volume and mass measurements
- determination of counting time and correction for dead time

- time measurements used in decay and ingrowth calculations
- approximation errors in simplified mathematical models
- published values for half-lives and radiation emission probabilities

NOTE: MARLAP does not recommend that laboratories expend tremendous effort on the evaluation of small components of uncertainty when much larger components are known to dominate the combined standard uncertainty of the result. However, this chapter does provide guidance in several places on the evaluation of very small uncertainties. Such examples may be instructive even if the uncertainties are negligible, because they illustrate either important concepts or possible methods of uncertainty evaluation. Furthermore, an uncertainty component that is negligible in one context (e.g., pipetting uncertainty in the context of measuring the activity of a radionuclide in a soil sample) may be considered significant in another (e.g., quality control of measuring instruments). It is also true that a very large number of small uncertainties may be significant when combined.

19.4.2 Evaluation of Standard Uncertainties

Calculating the combined standard uncertainty of an output estimate $y = f(x_1, x_2, \ldots, x_N)$ requires the evaluation of the standard uncertainty of each input estimate, x_i. As stated earlier, methods for evaluating standard uncertainties are classified as either "Type A" or "Type B." A Type A evaluation of an uncertainty uses a series of measurements to estimate the standard deviation empirically. Any other method of evaluating an uncertainty is a Type B method.

In general, the standard uncertainty of an input estimate, x_i, is an estimated standard deviation for the estimator whose value is used for x_i. The appropriate methods for estimating this standard deviation depend on how the value of the input estimate is obtained.

19.4.2.1 Type A Evaluations

Suppose X_i is an input quantity in the mathematical model. If a series of n independent observations of X_i are made under the same measurement conditions, yielding the results $X_{i,1}, X_{i,2}, \ldots, X_{i,n}$, the appropriate value for the input estimate x_i is the *arithmetic mean*, or *average*, $\overline{X}_i$, defined as

$$\overline{X}_i = \frac{1}{n} \sum_{k=1}^{n} X_{i,k} \tag{19.1}$$

The *experimental variance* of the observed values is defined as

$$s^2(X_{i,k}) = \frac{1}{n-1} \sum_{k=1}^{n} (X_{i,k} - \overline{X}_i)^2 \tag{19.2}$$

and the *experimental standard deviation*, $s(X_{i,k})$, is the square root of $s^2(X_{i,k})$. The *experimental standard deviation of the mean*, $s(\overline{X}_i)$, is obtained by dividing $s(X_{i,k})$ by $\sqrt{n}$.[6]

$$s(\overline{X}_i) = \frac{s(X_{i,k})}{\sqrt{n}} \tag{19.3}$$

The experimental standard deviation of the mean is also commonly called the "standard error of the mean."

The Type A standard uncertainty of the input estimate $x_i = \overline{X}_i$ is defined to be the experimental standard deviation of the mean. Combining the preceding formulas gives the following equation for the standard uncertainty of x_i:

$$u(x_i) = \sqrt{\frac{1}{n(n-1)} \sum_{k=1}^{n} (X_{i,k} - \overline{X}_i)^2} \tag{19.4}$$

When the input estimate x_i and standard uncertainty $u(x_i)$ are evaluated as described above, the number of *degrees of freedom* for the evaluation is equal to $n - 1$, or one less than the number of independent measurements of the quantity X_i. In general, the number of degrees of freedom for a statistical determination of a set of quantities equals the number of independent observations minus the number of quantities estimated. The number of degrees of freedom for each evaluation of standard uncertainty is needed to implement the procedure for calculating coverage factors described in Attachment 19D.

EXAMPLE 19.1 Ten independent measurements of a quantity X_i are made, yielding the values

12.132	12.139	12.128	12.133	12.132
12.135	12.130	12.129	12.134	12.136

The estimated value x_i is the arithmetic mean of the values $X_{i,k}$.

$$x_i = \overline{X}_i = \frac{1}{n} \sum_{k=1}^{n} X_{i,k} = \frac{121.328}{10} = 12.1328$$

[6] The experimental standard deviation of the mean, $s(\overline{X}_i)$, may be used as the standard uncertainty of the average, $\overline{X}_i$, even if the individual observations $X_{i,k}$ are obtained under different conditions of measurement, so long as all pairs of distinct observations, $X_{i,k}$ and $X_{i,\ell}$, can be considered to be uncorrelated. However, in these circumstances, it is sometimes better to define the input estimate, x_i, to be a *weighted* average of the observations.

The standard uncertainty of x_i is

$$u(x_i) = s(\overline{X}_i) = \sqrt{\frac{1}{n\,(n-1)} \sum_{k=1}^{n} (X_{i,k} - \overline{X}_i)^2}$$

$$= \sqrt{\frac{1}{10\,(10-1)} \sum_{k=1}^{10} (X_{i,k} - 12.1328)^2}$$

$$= \sqrt{1.12889 \times 10^{-6}} \quad = 0.0011$$

USE OF HISTORICAL DATA

In some cases there may be accumulated data for a measurement system, such as a balance or pipet, which can be used in a Type A evaluation of uncertainty for future measurements, assuming the measurement process remains in control. In fact the use of recent historical data is advisable in such cases, because it enlarges the pool of data available for uncertainty evaluation and increases the number of degrees of freedom. This type of uncertainty evaluation can be linked closely to the measurement system's routine quality control.

One may pool recent historical data with current measurement data, or one may evaluate an uncertainty based on historical data alone. The appropriate expression for the standard uncertainty depends on how the data are used to calculate the input estimate, x_i, and on whether x_i is used to *estimate* the value of a parameter or to *predict* the value of a variable. An example of estimating the value of a parameter is measuring the mass of material in a container using an analytical balance. An example of predicting the value of a variable is calibrating a pipet, since the actual volumes dispensed by the pipet in subsequent measurements vary and are seldom measured directly.

Attachment 19E provides descriptions and examples of the use of historical data for Type A evaluations of uncertainty in mass and volume measurements.

EVALUATION OF COVARIANCE

If X_i and X_j are two input quantities and estimates of their values are correlated, a Type A evaluation of covariance may be performed by making n independent pairs of simultaneous observations of X_i and X_j and calculating the experimental covariance of the means. If the observed pairs are $(X_{i,1},X_{j,1})$, $(X_{i,2},X_{j,2})$, …, $(X_{i,n},X_{j,n})$, the *experimental covariance* of the values is

$$s(X_{i,k},X_{j,k}) = \frac{1}{n-1}\sum_{k=1}^{n}(X_{i,k}-\overline{X}_i)(X_{j,k}-\overline{X}_j) \tag{19.5}$$

and the *experimental covariance of the means* $\overline{X}_i$ and $\overline{X}_j$ is

$$s(\overline{X}_i,\overline{X}_j) = \frac{s(X_{i,k},X_{j,k})}{n} \tag{19.6}$$

So, the Type A covariance of the input estimates $x_i = \overline{X}_i$ and $x_j = \overline{X}_j$ is

$$u(x_i,x_j) = s(\overline{X}_i,\overline{X}_j) = \frac{1}{n(n-1)}\sum_{k=1}^{n}(X_{i,k}-\overline{X}_i)(X_{j,k}-\overline{X}_j) \tag{19.7}$$

An evaluation of variances and covariances of quantities determined by the method of least squares may also be a Type A evaluation.

19.4.2.2 Type B Evaluations

There are many ways to perform Type B evaluations of standard uncertainty. This section describes some common Type B evaluations but is not meant to be exhaustive.

POISSON COUNTING UNCERTAINTY

One example of a Type B method already given is the estimation of counting uncertainty using the square root of the observed counts. If the observed count is N, when the Poisson approximation is used, the standard uncertainty of N may be evaluated as $u(N) = \sqrt{N}$. When N may be very small or even zero, MARLAP recommends the use of the equation $u(N) = \sqrt{N+1}$ instead (see Attachment 19D).

EXAMPLE 19.2 A Poisson counting measurement is performed, during which $N = 121$ counts are observed. So, the standard uncertainty of N is $u(N) = \sqrt{121} = 11$.

RECTANGULAR DISTRIBUTION

Sometimes a Type B evaluation of an uncertainty $u(x)$ consists of estimating an upper bound a for the magnitude of the error of x based on professional judgment and the best available information. If nothing else is known about the distribution of the measured result, then after a is estimated, the standard uncertainty may be calculated using the equation

$$u(x) = \frac{a}{\sqrt{3}} \tag{19.8}$$

which is derived from a statistical model in which the error has a *rectangular*, or *uniform*, distribution bounded by $-a$ and $+a$ (see Section 19A.6 in Attachment 19A).

EXAMPLE 19.3 The maximum error of a measured value $x = 34.40$ is estimated to be $a = 0.05$, with all values between 34.35 and 34.45 considered equally likely. So, the standard uncertainty of x is $u(x) = 0.05 / \sqrt{3} = 0.029$.

EXAMPLE 19.4 A strontium carrier solution is prepared by dissolving strontium nitrate in acidified water. The purity, P, of the strontium nitrate is stated to be 99.9 %, or 0.999, but no tolerance or uncertainty is provided. By default, a rectangular distribution with half-width $1 - P$, or 0.001, is assumed. So, the standard uncertainty of P is evaluated as $u(P) = 0.001 / \sqrt{3} = 0.00058$.

TRAPEZOIDAL DISTRIBUTION

It may also happen that one can estimate an upper bound, a, for the magnitude of the error so that the input quantity is believed with near certainty to lie between $x - a$ and $x + a$, but one believes that values near x are more likely than those near the extremes, $x \pm a$. In this case, a symmetric *trapezoidal* distribution may be used to obtain the standard uncertainty of x. The trapezoidal distribution is named for the fact that the graph of its pdf has the shape of a trapezoid (see Section 19A.7 in Attachment 19A). To use the trapezoidal model, one determines the value a, which represents the maximum possible error of the input estimate, and another value, β, which describes the fraction of possible values about the input estimate that are considered most likely ($0 < \beta < 1$). Then the standard uncertainty of x is given by the following expression.

$$u(x) = a\sqrt{\frac{1 + \beta^2}{6}} \tag{19.9}$$

As β approaches zero, the trapezoidal distribution becomes *triangular*, and the standard uncertainty of x approaches $a / \sqrt{6}$. As β approaches one, the trapezoidal distribution becomes rectangular, and the standard uncertainty of x approaches $a / \sqrt{3}$.

EXAMPLE 19.5 Extreme bounds for a quantity X are estimated to be 34.3 and 34.5, with values between 34.35 and 34.45 considered most likely. Using the trapezoidal model, one obtains the input estimate

$$x = \frac{34.3 + 34.5}{2}$$

the half-width

$$a = \frac{34.5 - 34.3}{2} = 0.1$$

and the fraction

$$\beta = \frac{34.45 - 34.35}{34.5 - 34.3} = \frac{0.1}{0.2} = 0.5$$

Then the standard uncertainty of x is calculated as follows.

$$u(x) = a\sqrt{\frac{1 + \beta^2}{6}} = 0.1\sqrt{\frac{1 + 0.5^2}{6}} = 0.046$$

EXAMPLE 19.6 The manufacturer of a 100-milliliter volumetric flask specifies that the capacity tolerance is 0.08 mL. The user of the flask assumes the tolerance represents the half-width of a triangular distribution and evaluates the standard uncertainty of the capacity to be $0.08 / \sqrt{6} = 0.033$ mL. (See Section 19.5.10 and Attachment 19E for more information about the uncertainty of a volume measurement.)

IMPORTED VALUES

When the estimate of an input quantity is taken from an external source, such as a book or a calibration certificate, which states the uncertainty as a multiple of the standard deviation s, the standard uncertainty is obtained by dividing the stated uncertainty by the stated multiplier of s.

EXAMPLE 19.7 The uncertainty for a measured activity concentration, c_A, is stated to be 0.015 Bq/L and the stated multiplier is 2. So, the standard uncertainty of c_A is $u(c_A) = 0.015 / 2 = 0.0075$ Bq/L.

If the estimate is provided by a source which gives a bound c for the error such that the interval from $x - c$ to $x + c$ contains the true value with 100γ % confidence ($0 < \gamma < 1$) but no other information about the distribution is given, the measured result may be assumed to have a normal distribution, and the standard uncertainty may therefore be evaluated as

$$u(x) = \frac{c}{z_{(1+\gamma)/2}} \tag{19.10}$$

The value of $z_{(1+\gamma)/2}$ may be found in a table of quantiles of the standard normal distribution (see Table G.1 in Appendix G).

EXAMPLE 19.8 The specific activity, x, of a commercial standard solution is stated to lie within the interval (4530 ± 64) Bq/g with 95 % confidence. The standard uncertainty may therefore be evaluated as $u(x) = 64 / z_{0.975} = 64 / 1.96 = 33$ Bq/g.

EVALUATION OF COVARIANCE

Evaluation of the covariance of two input estimates, x_i and x_j, whose uncertainties are evaluated by Type B methods may require expert judgment. Generally, in such cases it is simpler to estimate the correlation coefficient, $r(x_i,x_j)$, first and then multiply it by the standard uncertainties, $u(x_i)$ and $u(x_j)$ to obtain the covariance, $u(x_i,x_j)$. The correlation coefficient must be a number between −1 and +1. A correlation coefficient of zero indicates no correlation between the estimates, while a value of ±1 indicates the strongest possible correlation. Usually, if the two input estimates have a significant correlation, it is easy to guess the sign of the correlation coefficient, but estimating its magnitude may require knowledge and experience.

If the input estimates are imported values (e.g., from a published reference), the only practical method of evaluating their covariance is to use the correlation coefficient, if any, provided with the estimates. When no correlation coefficient is stated, the input estimates must be assumed to be uncorrelated.

In many cases when a correlation between two input estimates is suspected, the reason for the suspicion is that identifiable random or systematic effects in the measurement process are known to affect both estimates. It may be possible in such cases to include additional explicit variables in the mathematical model to account for those effects, eliminating the need for Type B covariance evaluations.

Sometimes two input estimates for one measurement model are explicitly calculated from other measured values. Section 19.4.4 shows how one may evaluate the covariance for two such calculated values.

19.4.3 Combined Standard Uncertainty

19.4.3.1 Uncertainty Propagation Formula

Consider the mathematical model $Y = f(X_1, X_2, \ldots, X_N)$. If $x_1, x_2, \ldots, x_N$ are measured values of the input quantities, X_i, and $y = f(x_1, x_2, \ldots, x_N)$ is the calculated value of the output quantity, Y, the combined standard uncertainty of y is obtained using the following formula.

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} u(x_i, x_j) \qquad (19.11)$$

Uncertainty Propagation Formula

Here $u^2(x_i)$ denotes the estimated variance of x_i, or the square of its standard uncertainty; $u(x_i, x_j)$ denotes the estimated covariance of x_i and x_j; $\partial f / \partial x_i$ (or $\partial y / \partial x_i$) denotes the partial derivative of f with respect to X_i evaluated at the measured values $x_1, x_2, \ldots, x_N$; and $u_c^2(y)$ denotes the combined variance of y, whose positive square root, $u_c(y)$, is the combined standard uncertainty of y. The partial derivatives, $\partial f / \partial x_i$, are called *sensitivity coefficients*.

The preceding formula, called the "law of propagation of uncertainty" in the *GUM*, will be called the "uncertainty propagation formula" or the "first-order uncertainty propagation formula" in this document. Equation 19.11 is commonly used to *define* the combined standard uncertainty, but note that the combined standard uncertainty is only an approximation of the true standard deviation of the output estimate, and sometimes other definitions provide better approximations (e.g., see Section 19.4.5.1).[7]

Table 19.1 shows several rules for partial differentiation, which tend to be useful when one calculates the sensitivity coefficients in the uncertainty propagation formula. Table 19.2 shows how to propagate uncertainties in some common cases. The expressions for the combined standard uncertainties shown in Table 19.2 may be derived from the uncertainty propagation formula using the differentiation rules listed in Table 19.1.

[7] The uncertainty propagation formula may be derived by approximating the function f by a first-order Taylor polynomial.

TABLE 19.1 — Differentiation rules

In the following equations the symbols F and G denote arbitrary expressions, which may contain the variables $x_1, x_2, \ldots, x_N$. The symbol c denotes either a constant expression or any other expression that does not contain the variable x_i.

$$\frac{\partial c}{\partial x_i} = 0 \qquad \frac{\partial (F \pm G)}{\partial x_i} = \frac{\partial F}{\partial x_i} \pm \frac{\partial G}{\partial x_i} \qquad \frac{\partial (F^c)}{\partial x_i} = cF^{c-1}\frac{\partial F}{\partial x_i}$$

$$\frac{\partial x_i}{\partial x_i} = 1 \qquad \frac{\partial (FG)}{\partial x_i} = \frac{\partial F}{\partial x_i}G + F\frac{\partial G}{\partial x_i} \qquad \frac{\partial (\mathrm{e}^F)}{\partial x_i} = \mathrm{e}^F\frac{\partial F}{\partial x_i}$$

$$\frac{\partial x_j}{\partial x_i} = 0, \text{ if } i \neq j \qquad \frac{\partial (F/G)}{\partial x_i} = \frac{(\partial F/\partial x_i)G - F(\partial G/\partial x_i)}{G^2} \qquad \frac{\partial (\ln F)}{\partial x_i} = \frac{\partial F/\partial x_i}{F}$$

$$\frac{\partial (cF)}{\partial x_i} = c\frac{\partial F}{\partial x_i} \qquad \frac{\partial (1/F)}{\partial x_i} = \frac{-\partial F/\partial x_i}{F^2} \qquad \frac{\partial (\log_{10} F)}{\partial x_i} = \frac{\partial F/\partial x_i}{(\ln 10)F}$$

TABLE 19.2 — Applications of the first-order uncertainty propagation formula

SUMS AND DIFFERENCES	If a and b are constants, then $$u_c^2(ax \pm by) = a^2u^2(x) + b^2u^2(y) \pm 2ab \cdot u(x,y)$$
PRODUCTS	If x and y are measured values, then $$u_c^2(xy) = u^2(x)y^2 + x^2u^2(y) + 2xy \cdot u(x,y)$$ When x and y are nonzero, the formula may be rewritten as $$u_c^2(xy) = x^2y^2\left(\frac{u^2(x)}{x^2} + \frac{u^2(y)}{y^2} + \frac{2u(x,y)}{xy}\right)$$
QUOTIENTS	If x and y are measured values, then $$u_c^2\left(\frac{x}{y}\right) = \frac{u^2(x)}{y^2} + \frac{x^2u^2(y)}{y^4} - \frac{2x \cdot u(x,y)}{y^3}$$ When x is nonzero, the variance formula may be rewritten as $$u_c^2\left(\frac{x}{y}\right) = \frac{x^2}{y^2}\left(\frac{u^2(x)}{x^2} + \frac{u^2(y)}{y^2} - \frac{2u(x,y)}{xy}\right)$$
EXPONENTIALS	If a is a constant, then $$u_c^2(\mathrm{e}^{ax}) = a^2\mathrm{e}^{2ax}u^2(x)$$ If n is a positive integral constant, then $$u_c^2(x^n) = n^2x^{2n-2}u^2(x)$$
LOGARITHMS	If a is a constant and ax is positive, then $$u_c^2(\ln ax) = \frac{u^2(x)}{x^2} \quad \text{and} \quad u_c^2(\log_{10} ax) = \frac{u^2(x)}{(\ln 10)^2x^2} \approx \frac{u^2(x)}{(5.302)x^2}$$

$$\frac{\partial q}{\partial x} = \frac{1}{y} \qquad \frac{\partial^2 q}{\partial x^2} = 0 \qquad \frac{\partial^3 q}{\partial x^3} = 0$$

$$\frac{\partial q}{\partial y} = -\frac{x}{y^2} \qquad \frac{\partial^2 q}{\partial y^2} = \frac{2x}{y^3} \qquad \frac{\partial^3 q}{\partial y^3} = -\frac{6x}{y^4}$$

$$\frac{\partial^2 q}{\partial x\,\partial y} = -\frac{1}{y^2} \qquad \frac{\partial^3 q}{\partial x\,\partial y^2} = \frac{2}{y^3} \qquad \frac{\partial^3 q}{\partial y\,\partial x^2} = 0$$

$$u_c^2(q) = \frac{u^2(x)}{y^2} + q^2\frac{u^2(y)}{y^2} + 0 \times u^4(x) + \left(\frac{1}{2}\left(-\frac{1}{y^2}\right)^2 + \left(\frac{1}{y}\right)\left(\frac{2}{y^3}\right)\right) u^2(x)\,u^2(y)$$
$$+ \left(\frac{1}{2}\left(-\frac{1}{y^2}\right)^2 + 0\right) u^2(y)\,u^2(x) + \left(\frac{1}{2}\left(\frac{4x^2}{y^6}\right) + \left(-\frac{x}{y^2}\right)\left(-\frac{6x}{y^4}\right)\right) u^4(y)$$
$$= \frac{u^2(x)}{y^2}\left(1 + 3\frac{u^2(y)}{y^2}\right) + q^2\frac{u^2(y)}{y^2}\left(1 + 8\frac{u^2(y)}{y^2}\right)$$

With numbers,

$$u_c(q) = \sqrt{\frac{0.5^2}{10^2}\left(1 + 3\frac{3^2}{10^2}\right) + 0.5^2\frac{3^2}{10^2}\left(1 + 8\frac{3^2}{10^2}\right)} = 0.205$$

In this case, since 0.205 is substantially larger than 0.158, the first-order formula is inadequate.

If the standard uncertainty of y is much larger than 3 (in this case 30 % in relative terms), even the higher-order formula begins to fail here.

19.4.5.2 Bias due to Nonlinearity

As noted earlier, when the measurement model has the form $Y = f(X_1,X_2,\ldots,X_N)$ and the input estimates are $x_1, x_2, \ldots, x_N$, the output estimate is given by $y = f(x_1,x_2,\ldots,x_N)$. If the function, f, is nonlinear, the output estimate, y, may be a biased estimate of the value of the output quantity, Y, even if the model is correct and each of the input estimates, x_i, is an unbiased estimate of the associated input quantity (Ku, 1966).

For example, if the model is $Y = f(X) = X^2$ and X is an unbiased estimator for some quantity θ, then $Y = X^2$ is a biased estimator for the quantity θ^2. (I.e., the mean of the square is not equal to the square of the mean.) Since the variance of X is $V(X) = E(X^2) - E(X)^2$ and the mean of X is $E(X) = \theta$, the mean of Y in this case is given by

$$E(Y) = E(X^2) = E(X)^2 + V(X) = \theta^2 + V(X) \tag{19.20}$$

So, the bias of $Y = X^2$ as an estimator for θ^2 is equal to the variance of X. In metrology the true variance of the estimator X is unknown of course, but the bias of an output estimate, $y = x^2$, can be estimated by $u^2(x)$, the square of the standard uncertainty of the input estimate, x.

More generally, the portion of the bias of y associated with the nonlinearity of the model may be estimated, if necessary, by the formula

$$\text{Bias}(y) \approx \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\partial^2 f}{\partial x_i \partial x_j}u(x_i, x_j) \tag{19.21}$$

In practice, Equation 19.21 is equivalent to the following (Ku, 1966).

$$\text{Bias}(y) \approx \frac{1}{2}\sum_{i=1}^{N}\frac{\partial^2 f}{\partial x_i^2}u^2(x_i) + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{\partial^2 f}{\partial x_i \partial x_j}u(x_i, x_j) \tag{19.22}$$

This bias is usually negligible in comparison to the combined standard uncertainty, $u_c(y)$, if the relative standard uncertainty of each input estimate is small. (These equations are based on an approximation of the function f by a second-order Taylor polynomial.)

Note that the bias calculated by Equations 19.21 and 19.22 may not represent the overall bias of the output estimate. It represents only the bias associated with nonlinearity of the mathematical model. If the input estimates are biased or the model is inexact, the overall bias may be different.

MARLAP does not recommend correcting the output estimate for the estimated bias due to non-linearity. Instead, the standard uncertainties of the input estimates should be kept small enough to make this portion of the bias negligible. For a typical radiochemical measurement model involving a net count rate divided by a denominator consisting of a product of factors such as the counting efficiency, test portion size, and chemical yield, this requirement means keeping the uncertainties of the counting times and all the factors in the denominator relatively small. The relative uncertainties of the raw counts may be large.

EXAMPLE 19.13 If x is an estimate of a positive quantity X, the bias of $y = 1 / x$ as an estimate of $1 / X$ may be approximated using Equation 19.22. Since y is a function of only one variable, the partial derivatives of y are the same as ordinary derivatives. The first derivative is $dy/dx = -x^{-2}$ and the second derivative is $d^2y/dx^2 = 2x^{-3}$. So, the bias due to nonlinearity can be estimated as $\text{Bias}(y) \approx (1/2)(2x^{-3})u^2(x) = u^2(x)/x^3$.

Suppose $x = 1.2$ and its standard uncertainty is 0.2. Then the calculated value of y is 1 / 1.2, or 0.833, and the estimated bias of y due to nonlinearity is $0.2^2 / 1.2^3 = 0.023$.

EXAMPLE 19.14 If x and y are uncorrelated, unbiased estimates of quantities X and Y, respectively, the bias of the product $z = xy$ as an estimate of XY is given approximately by

$$\text{Bias}(z) \approx \frac{1}{2}\left(\frac{\partial^2 z}{\partial x^2} u^2(x) + \frac{\partial^2 z}{\partial y^2} u^2(y) \right)$$

which equals zero, since $\partial^2 z / \partial x^2 = \partial^2 z / \partial y^2 = 0$. (In this case, it can be shown that the bias of z is exactly zero, not just approximately zero.)

EXAMPLE 19.15 If t is an estimate of the decay time T for a radionuclide whose decay constant is λ (assumed to have negligible uncertainty), the bias of the estimated decay factor $D = e^{-\lambda t}$ is given approximately by

$$\text{Bias}(D) \approx \frac{1}{2}\frac{\partial^2 D}{\partial t^2} u^2(t) = \frac{1}{2}\lambda^2 e^{-\lambda t} u^2(t)$$

and the relative bias is $\lambda^2 u^2(t) / 2$. For example, suppose the radionuclide is ^{228}Ac, which has a half-life of $T_{1/2} = 6.15$ h, and the decay time has a standard uncertainty of $u(t) = 2$ h (large for the sake of illustration). Then the decay constant λ equals $\ln(2) / 6.15 = 0.112707$ h^{-1}. The bias equation above implies that the relative bias of the decay factor D due to the uncertainty of t is approximately

$$\frac{\text{Bias}(D)}{D} \approx \frac{1}{2}\lambda^2 u^2(t) = \frac{1}{2}(0.112707)^2 (2)^2 = 0.025$$

or 2.5 %. Note that the relative bias of D is small if $u^2(t) / T_{1/2}^2$ is small. (In this example, $u^2(t) / T_{1/2}^2 = 2^2 / 6.15^2 = 0.1058$.)

19.4.6 Monte Carlo Methods

An alternative to uncertainty propagation is the use of computerized Monte Carlo methods to propagate not the uncertainties of input estimates but their distributions. Given assumed distributions for the input estimates, the method provides an approximate distribution for the output estimate, from which the combined standard uncertainty or an uncertainty interval may be derived. The joint working group responsible for the *GUM* is reported to be developing new guidance on the use of such methods. Monte Carlo methods may be particularly useful when the distribution of the result is not approximately normal. However, these methods are most effective when the model can be formulated in terms of independent input estimates.

19.5 Radiation Measurement Uncertainty

19.5.1 Radioactive Decay

Although it is impossible to know when an unstable nucleus will decay, it is possible to calculate the probability of decay during a specified time interval. The lifetime of the nucleus has an *exponential distribution*, which is a model for the life of any object whose expected remaining life does not change with age.

The exponential distribution is described by one parameter λ, which measures the expected fractional decay rate. This parameter λ is called the *decay constant* and equals $\ln(2) / T_{1/2}$, or approximately $0.693 / T_{1/2}$, where $T_{1/2}$ is the half-life of the radionuclide (sometimes denoted by $t_{1/2}$). The half-life is the same as the median of the exponential distribution.

The probability that an atom will survive until time t without decaying is equal to $e^{-\lambda t}$. Thus the probability of survival decreases exponentially with time. Consequently, when a large number of atoms of the same radionuclide are considered, the expected number of surviving atoms also decreases exponentially with time, as shown in Figure 19.2.

Since the probability that an atom survives until time t is equal to $e^{-\lambda t}$, it follows that the probability of decay during this time is $1 - e^{-\lambda t}$.

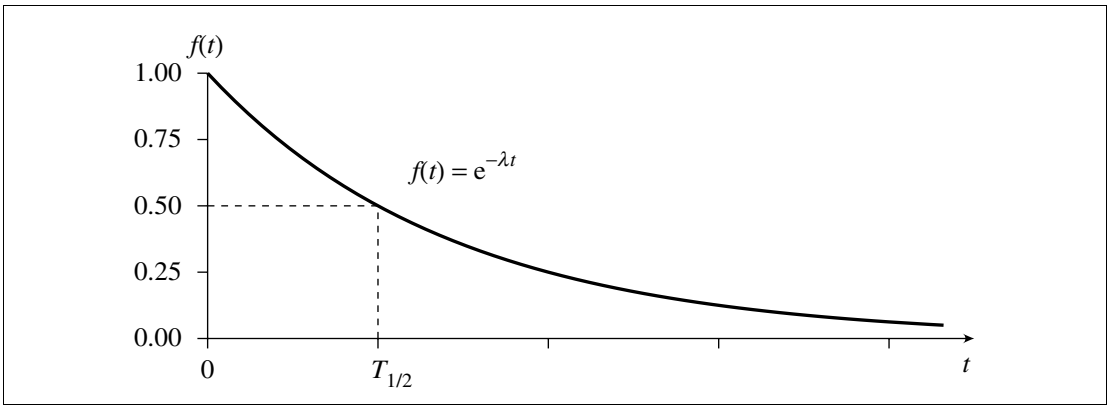

FIGURE 19.2 — Expected fraction of atoms remaining at time *t*

19.5.2 Radiation Counting

Undoubtedly the best-known rule of radiation measurement statistics is the fact that the counting uncertainty for a gross radiation measurement can be evaluated as the square root of the observed counts. The square-root rule is useful, because it permits the estimation of a potentially significant uncertainty component without replicate measurements. Although the rule is usually valid as an approximation, for reasons which are discussed below, there are limits to its applicability. It is also important to remember that the counting uncertainty is only one component of the total measurement uncertainty.

19.5.2.1 Binomial Model

When a source containing a radionuclide is placed in a detector, the probability that a particular atom of the radionuclide will produce a count is the product of three factors: the probability of decay, the probability of emission of the radiation being measured, and the probability of detection. According to the exponential decay model, the probability of decay is equal to $1 - e^{-\lambda t_S}$, where λ is the decay constant and t_S is the counting time. The probability of radiation emission, denoted here by F, is a characteristic of the radionuclide. The probability of detection is the counting efficiency, ε. Then the probability that an atom will generate a count is $p = (1 - e^{-\lambda t_S})F\varepsilon$.

If the source initially contains n atoms of the radionuclide, the instrument is stable, and its background is negligible, the number of observed counts N has a *binomial distribution with parameters n and p*. In general, if an experiment has only two possible outcomes, which may be called "success" and "failure," and the probability of success is p, then the number of successes observed when the experiment is repeated in n independent trials has a binomial distribution with parameters n and p.

Actually the probability p is a random variable, because the counting efficiency for an instrument and source can vary for a number of reasons, such as source placement, dead time and other instrument characteristics. These variations generate measurement uncertainty, but their effects are not included in the "counting uncertainty." The counting uncertainty is the standard deviation of the *theoretical* distribution of counts observed in a fixed time period when the efficiency is held constant. *Thus, the actual variability observed in repeated measurements of a single radioactive source may be greater than the theoretical counting uncertainty*.

19.5.2.2 Poisson Approximation

The mean and variance of the binomial distribution are np and $np(1 - p)$, respectively. In radiation counting, the value of p is usually small enough that the factor $1 - p$ in the variance can be ignored (i.e., treated as 1). When this is true, the binomial distribution can be approximated by a *Poisson distribution* with mean $\mu = np$. The variance of a Poisson distribution equals the mean; so, both can be estimated by the same measured result N, and the standard deviation can be estimated by $\sqrt{N}$.[10]

When μ is large, $\sqrt{N}$ is an excellent estimator for the standard deviation, σ_N, but the estimate may be poor when μ is small. For example, if $\mu = 100$, the coefficient of variation of $\sqrt{N}$ is only about 5 % and its bias (caused by the nonlinearity of the square-root function) is negligible.[11] If $\mu = 10$, the coefficient of variation is more than 16 % and there is a negative bias of more than 1 %. If $\mu = 1$, the coefficient of variation is more than 63 % and the negative bias is more than 22 %. Furthermore, when μ is small, it is possible to observe zero counts, so that $\sqrt{N} = 0$. MARLAP recommends that $\sqrt{N}$ be replaced by $\sqrt{N + 1}$ when extremely low counts are possible (see also Attachment 19D).[12]

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[10] In the rare cases when the Poisson model is inadequate and the binomial model is required, if the instrument background level is negligible, the standard deviation of the source count N_S can be estimated by $\sqrt{(1-p)N_S}$. If the background is not negligible, the variance of N_S is the sum of components contributed by the background and the source. So, if a Poisson background is measured for time t_B and N_B counts are observed, the background contribution to N_S is estimated by $N_B t_S / t_B$, and the source contribution is estimated by $(N_S - N_B t_S / t_B)$. Then the standard deviation of N_S may be estimated by combining the estimated variances of these two contributions, as shown below.

$$\sigma_{N_S} \approx \sqrt{N_B \frac{t_S}{t_B} + \left(N_S - N_B \frac{t_S}{t_B} \right) (1 - p)} = \sqrt{(1-p) N_S + p N_B \frac{t_S}{t_B}}$$

These expressions for the standard deviation of N_S are appropriate only when the source counts are generated by a single radionuclide or by one radionuclide plus the instrument background.

[11] The coefficient of variation of a nonnegative random variable is defined as the ratio of its standard deviation to its mean (see Attachment 19A).

[12] The negative bias of $\sqrt{N}$ as an estimator for σ_N is largely eliminated if one replaces it by $\sqrt{N + 0.25}$. MARLAP recommends the estimator $\sqrt{N + 1}$ although it is positively biased.

A sum of independent Poisson quantities also has a Poisson distribution. So, when the Poisson approximation is valid for all the sources of counts in a counting measurement, the total count obeys Poisson counting statistics as well.

If a short-lived radionuclide (large λ) is counted in a high-efficiency detector (large ε), the probability p that an atom placed in the detector will produce a count may be so large that the Poisson approximation is invalid. In this case the Poisson approximation overestimates the counting uncertainty; however, it is important to consider that the statistical model described thus far represents only the process of counting. In most cases previous steps in the measurement process decrease the probability that one of the atoms of interest initially present in the test portion (the portion of sample taken for analysis) will produce a count. If a correction for decay before counting is performed, the decay factor must be included in p. If the measured activity of a (single) decay product is used to estimate the activity of a parent, p must include both ingrowth and decay factors. If a chemical extraction is performed, the recovery factor must be considered. When these factors are included, the Poisson model is usually valid. Note, however, that these factors must be measured and their standard uncertainties evaluated and propagated, increasing the total measurement uncertainty even further.[13]

Both the binomial and Poisson models may be invalid if one atom can produce more than one count during the measurement. This situation occurs when the activity of a parent is estimated from the total count produced by the parent and a series of short-lived progeny (Lucas and Woodward, 1964; Collé and Kishore, 1997). For example when ^{222}Rn is measured by counting the emissions of the parent and its progeny, an atom of ^{222}Rn may produce several counts as it decays through the short-lived series ^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po, to the longer-lived ^{210}Pb. Another example is the measurement of ^{234}Th by beta-counting a source that contains ^{234}Th and its short-lived progeny, ^{234m}Pa.

Both counting models may also be invalid if the total dead time of the measurement is significant (see Section 19.5.3.1).

Instrument background measurements are usually assumed to follow the Poisson model. This assumption is reasonable if the background counts are produced by low levels of relatively long-lived radionuclides. However, the true background may vary between measurements (e.g., cosmic background). Furthermore, the measured background may include spurious instrument-generated counts, which do not follow a Poisson distribution. Generally, the variance of the observed background is somewhat greater than the Poisson counting variance, although it may be

[13] It is possible to evaluate the uncertainties associated with the decay and ingrowth of a small number of short-lived atoms before counting using the binomial model, but under the stated conditions, the assumption of Poisson counting statistics simplifies the calculation. A more complete evaluation of uncertainty may be necessary if the same source is counted more than once.

less for certain types of instruments, such as those that use parallel coincidence counters to compensate for background instability (Currie et al., 1998). Departures from the Poisson model may be detected using the chi-squared test described in Section 18B.2 of Attachment 18B; however, deviations from the model over short time periods may be small and difficult to measure.

19.5.3 Count Time and Count Rate

Suppose a radiation counting measurement of duration t is made for the purpose of estimating a mean count rate r, assumed to be constant, and the result of the measurement (in counts) has a distribution that is approximately Poisson with mean rt. If t is known precisely, the best estimate of r given a single observation, N, is the measured count rate $R = N / t$, and the best estimate of the variance of the measured rate is $u^2(R) = N / t^2 = R / t$. Under the Poisson assumption, even if repeated measurements are made, the best estimates of the count rate and its variance are obtained by pooling the counts and count times and using the same formulas.

In fact, the count time t is known imperfectly; so a more complete estimate of the variance of R is

$$u^2(R) = \frac{N}{t^2} + \frac{N^2}{t^4} u^2(t) \tag{19.23}$$

The uncertainty of t may be ignored if $u(t) / t \ll 1 / \sqrt{N}$, that is, if the relative standard uncertainty of t is much less than 1 over the square root of the count.

EXAMPLE 19.16 A source is counted for $t = 100$ s, where t has standard uncertainty $u(t) = 0.1$ s, and $N = 25$ counts are observed. Thus, the observed count rate, R, equals 0.250 s^{-1}. When $u(t)$ is ignored, the combined standard uncertainty of R is $u_c(R) = \sqrt{N / t^2} = 0.050$ s^{-1}. When $u(t)$ is included, the combined standard uncertainty is

$$u_c(R) = \sqrt{\frac{N}{t^2} + \frac{N^2}{t^4} u^2(t)} = \sqrt{\frac{25}{100^2} + \frac{25^2}{100^4} 0.1^2} \approx 0.050 \text{ s}^{-1}$$

In this case the difference between the two uncertainty estimates is negligible.

EXAMPLE 19.17 A source is counted for $t = 100$ s, where $u(t) = 1$ s, and $N = 10{,}609$ counts are observed. The count rate, R, equals N / t, or 106.09 s^{-1}. When $u(t)$ is ignored, $u_c(R) = \sqrt{N / t^2} =$ 1.03 s^{-1}. When $u(t)$ is included,

$$u_c(R) = \sqrt{\frac{N}{t^2} + \frac{N^2}{t^4}u^2(t)} = \sqrt{\frac{10{,}609}{100^2} + \frac{10{,}609^2}{100^4}1^2} \approx 1.48 \text{ s}^{-1}$$

In this example the two uncertainty estimates are clearly different, although both are relatively small (1 % to 1.4 %).

Sometimes a radiation counter is set to acquire a predetermined number of counts. In this case the number of counts is a constant and only the count time varies. If the mean count rate does not change appreciably during the measurement, then Equation 19.23 may still be used.[14]

19.5.3.1 Dead Time

The *dead time* for a counting instrument is the minimum separation, τ, between two events required for the instrument to process and record both. Theoretical models for dead time are generally of two types. If the dead time for one event may be extended by a second event that arrives before the first has been processed, the system is called "paralyzable" and the dead time is called "extendable." Otherwise, the system is called "non-paralyzable" and the dead time is called "non-extendable" (Knoll, 1989; Turner, 1995; NCRP, 1985). Both models are idealized. The behavior of an actual counting system tends to fall between the two extremes. At low count rates, however, both models give essentially the same predictions.

At low count rates the observed count rate, N / t, may be corrected for dead time by dividing by the factor $1 - N\tau / t$. Many counting instruments perform the correction automatically by extending the real time t of the measurement to achieve a desired live time, t_L. Since $t_L = t - N\tau$, the corrected count rate is simply N / t_L. When the dead time rate for the measurement is low, the variance of the corrected count rate may be estimated as N / t_L^2. Thus, the Poisson model remains adequate if the "count time" is equated with the live time. When the dead time rate is high (above 20 %), the same estimate may not be adequate (NCRP, 1985). In this case the measurement should be repeated, if possible, in a manner that reduces the dead time rate.

Dead time effects may be evaluated experimentally to confirm that they do not invalidate the Poisson model at the count rates expected for typical measurements. The chi-squared test described in Section 18B.2 of Attachment 18B can be used for this purpose.

[14] If the mean count rate, r, is constant, the waiting times between events are independent exponentially distributed random variables with parameter $\lambda = r$. Therefore, the total time required to obtain n counts is the sum of the n waiting times, which has a *gamma distribution* with parameters $\alpha = n$ and $\lambda = r$ (or $\alpha = n$ and $\beta = 1/\lambda = 1/r$).

19.5.3.2 A Confidence Interval for the Count Rate

When the Poisson model of radiation counting is valid, lower and upper confidence limits for the mean count rate r given an observation of N counts in time t may be calculated as follows:[15]

$$r_{\text{lower}} = \chi^2_{(1-\gamma)/2}(2N) \,/\, 2t$$
$$r_{\text{upper}} = \chi^2_{(1+\gamma)/2}(2N + 2) \,/\, 2t \qquad (19.24)$$

Here γ is the desired *confidence coefficient*, or the minimum probability of coverage, and for any v, $\chi^2_p(v)$ denotes the p-quantile of the chi-squared distribution with v degrees of freedom (see Table G.3 in Appendix G). If $v = 0$, the chi-squared distribution $\chi^2(v)$ is degenerate. For our purposes, $\chi^2_p(0)$ should be considered to be 0.

EXAMPLE 19.18 Suppose 10 counts are observed during a 600-second instrument background measurement. Then the 95 % confidence limits for the background count rate are

$$r_{\text{lower}} = \frac{\chi^2_{0.025}(20)}{(2)(600)} = \frac{9.59078}{1200} = 0.00799 \text{ s}^{-1}$$
$$r_{\text{upper}} = \frac{\chi^2_{0.975}(22)}{(2)(600)} = \frac{36.7807}{1200} = 0.03065 \text{ s}^{-1}$$

EXAMPLE 19.19 Suppose 0 counts are observed during a 600-second measurement. Then the 95 % confidence limits for the count rate are

$$r_{\text{lower}} = \frac{\chi^2_{0.025}(0)}{(2)(600)} = 0 \text{ s}^{-1}$$
$$r_{\text{upper}} = \frac{\chi^2_{0.975}(2)}{(2)(600)} = \frac{7.3778}{1200} = 0.00615 \text{ s}^{-1}$$

[15] The chi-squared distribution is a special case of a gamma distribution, whose relationship to the Poisson distribution is described by Hoel et al. (1971) and Stapleton (1995). This relationship is the basis for the two formulas in Equation 19.24. The relationship is such that if X is chi-squared with $2N$ degrees of freedom and Y is Poisson with mean μ, then $\Pr[X \le 2\mu] = \Pr[Y \ge N]$.

19.5.4 Instrument Background

As noted above, single-channel background measurements are usually assumed to follow the Poisson model, although there may be effects which increase the variance beyond what the model predicts. For example, cosmic radiation and other natural sources of instrument background may vary between measurements, the composition of source holders and containers may vary, the instrument may become contaminated by sources, or the instrument may simply be unstable. For certain types of instruments, the Poisson model may overestimate the background variance (Currie et al., 1998). If the background does not closely follow the Poisson model, its variance should be estimated by repeated measurements.

The "instrument background," or "instrument blank," is usually measured with source holders or containers in place, since the presence of the container may affect the count rate. In many cases, perhaps most, it is not feasible to use the same container during both the background and test source measurements, but nearly identical containers should be used. Variations in container composition may affect the background count rate. If test sources contain enough mass to attenuate background radiation, then it is best to use a similar amount of blank material during the background measurement.

If repeated measurements demonstrate that the background level is stable, then the average, $\overline{x}$, of the results of many similar measurements performed over a period of time may give the best estimate of the background. In this case, if all measurements have the same duration, the experimental standard deviation of the mean, $s(\overline{x})$, is also a good estimate of the measurement uncertainty. Given the Poisson assumption, the best estimate of the uncertainty is still the Poisson estimate, which equals the square root of the summed counts, divided by the number of measurements, but the experimental standard deviation may be used when the Poisson assumption is invalid.

If the background drifts or varies nonrandomly over time (i.e., is nonstationary), it is important to minimize the consequences of the drift by performing frequent blank measurements.

If the background variance includes a small non-Poisson component, that component can be estimated from historical background data and added to the calculated Poisson component. A chi-squared statistic may be used to detect and quantify non-Poisson background variance (Currie, 1972; see also Section 18B.3 of Attachment 18B), but chi-squared provides an unbiased estimate of the additional variance only if the background remains stationary while the data are being collected. If the observed background counts, in order, are $N_1, N_2, \ldots, N_n$ and the corresponding counting intervals are $t_1, t_2, \ldots, t_n$, then the quantity

$$\xi_B^2 = \frac{1}{n-1}\sum_{i=1}^{n-1}\left[\left(\frac{N_{i+1}}{t_{i+1}} - \frac{N_i}{t_i}\right)^2 - \frac{N_i + N_{i+1}}{t_i t_{i+1}}\right] \tag{19.25}$$

may be used to estimate the non-Poisson variance of a net count rate due to background even if the background is not stationary.[16] The distribution of ξ_B^2 is not simple, and ξ_B^2 may even assume negative values, which are clearly unrealistic. So, if this estimator is used, it should be calculated for several data sets and for more than one instrument, if possible, to give an indication of its reliability. Although replicate measurements are involved, this type of evaluation of uncertainty should be considered a Type B method.

If background and test source measurements are performed under different conditions, the background measurement may be biased. Such a bias may occur, for example, if test sources are counted in containers or on planchets which are not present during background measurements. A situation of this kind should be avoided if possible.

When instrument background levels are low or when count times are short, it is possible that too few counts will be observed to provide an accurate estimate of the measurement uncertainty. Attachment 19D describes a method for choosing an appropriate coverage factor when only few counts are observed.

19.5.5 Radiochemical Blanks

Instrument background is only one of the sources of counts observed when an analyte-free sample is analyzed. Other sources may include contaminants in the tracers, reagents, and glassware used for measurements. Contamination of this type tends to be most significant when the analytes are naturally occurring radionuclides, such as isotopes of uranium, thorium, and radium; but nonnatural contaminants may also be present in some radiochemical tracers.

The level of contamination may be determined by analyzing reagent blanks or other process blanks alongside laboratory samples (see Chapter 18). Alternatively, if the contaminant is present in a specific reagent or tracer solution, its concentration in the solution may be measured and incorporated into the mathematical model of the measurement. Regardless of which method of evaluation is used, it is important to remember that the concentration of contaminant may vary from one reagent lot to another, and that the amount of contaminant in the prepared source may

[16] Each term of the sum is an unbiased estimator for the non-Poisson variance of the difference between successive measurements of the background. Note that $(N_{i+1}/t_{i+1} - N_i/t_i)^2$ is an unbiased estimator for the total variance and $(N_i + N_{i+1})/t_i t_{i+1}$, which equals $(N_i + N_{i+1})/(t_i + t_{i+1}) \times (1/t_i + 1/t_{i+1})$, is an unbiased estimator for the Poisson variance.

be affected by incomplete recovery during the chemical separation and purification steps of the analytical process.

If the amount of blank contaminant varies between measurements (e.g., because the analyte is present at varying levels in the laboratory environment), it is usually necessary to determine the blank level and its uncertainty by replicate measurements (a Type A evaluation). *In this case, using the pure Poisson model for the uncertainty of the blank correction is inappropriate*. Replicate measurements are also more appropriate if the causes of blank contamination are simply not well understood.

If there is no observable contamination when analyte-free samples are analyzed, the radiochemical blank may be only a blank source, which mimics the geometry and composition of an actual test source. In this case the laboratory should routinely analyze method blanks to check for contamination (see Chapter 18) and take corrective action if contamination is found.

19.5.6 Counting Efficiency

The counting efficiency for a measurement of radioactivity (usually defined as the detection probability for a particle or photon of interest emitted by the source) may depend on many factors, including source geometry, placement, composition, density, activity, radiation type and energy and other instrument-specific factors. The estimated efficiency is sometimes calculated explicitly as a function of such variables (in gamma-ray spectrometry, for example). In other cases a single measured value is used (e.g., alpha-particle spectrometry). If an efficiency function is used, the uncertainties of the input estimates, including those for both calibration parameters and sample-specific quantities, must be propagated to obtain the combined standard uncertainty of the estimated efficiency. Calibration parameters tend to be correlated; so, estimated covariances must also be included. If a single value is used instead of a function, the standard uncertainty of the value is determined when the value is measured.

EXAMPLE 19.20 Fifteen sources in the same geometry are prepared from a standard solution and used to calibrate a radiation counter. The specific activity of the standard is 150.0 Bq/g with a combined standard uncertainty of 2.0 Bq/g. The steps of the calibration are as follows:

1. A 1-milliliter aliquant of the standard solution is added by pipet to each source and weighed on an analytical balance. The solution contains the radionuclide of interest dissolved in 0.3 M nitric acid, whose density at the current room temperature is 1.0079 g/mL. The density of the solution is used only to calculate the buoyancy-correction factor for the mass measurements, which equals 1.001028 in this case (see Attachment 19E). The uncertainties of the buoyancy-corrected masses are considered negligible.

2. A blank measurement is made. The blank count time is 6000 s. The number of blank counts observed is 87.
3. Each source is counted once on the instrument for 300 s.

The radionuclide is long-lived; so, no decay corrections are needed. The uncertainties of the count times are assumed to be negligible.

The mathematical model for the calibration is:

$$\varepsilon = \frac{1}{n}\sum_{i=1}^{n}\frac{N_{S,i}/t_S - N_B/t_B}{m_i a_S}$$

where

ε	is the counting efficiency;
n	is the number of sources (15);
$N_{S,i}$	is the gross count observed during the measurement of the i^{th} source;
t_S	is the source count time (300 s);
N_B	is the observed blank count (87);
t_B	is the blank count time (6000 s);
m_i	is the mass of standard solution added to the i^{th} source; and
a_S	is the specific activity of the standard solution (150.0 Bq/g).

For the purpose of uncertainty evaluation, it is convenient to rewrite the model as

$$\varepsilon = \frac{\overline{R}}{a_S}$$

where

$$\overline{R} = \frac{1}{n}\sum_{i=1}^{N} R_i \qquad \text{and} \qquad R_i = \frac{N_{S,i}/t_S - N_B/t_B}{m_i}, \quad i = 1, 2, ..., n$$

The values R_i and their average, $\overline{R}$, are estimates of the count rate produced by 1 g of the standard solution, while $\overline{R}/a_S$ is an estimate of the count rate produced by 1 Bq of activity. The standard uncertainty of $\overline{R}$ can be evaluated experimentally from the 15 repeated measurements. Since only one blank measurement is made, the input estimates R_i are correlated with each other. The covariance between R_i and R_j, for $i \neq j$, may be estimated as

$$u(R_i, R_j) = \frac{\partial R_i}{\partial N_B}\frac{\partial R_j}{\partial N_B}u^2(N_B) = \frac{-1}{t_B m_i}\frac{-1}{t_B m_j}u^2(N_B) = \frac{u^2(N_B)}{t_B^2 m_i m_j}$$

However, the correlation is negligible here because the uncertainty of the blank count, N_B, is much smaller than the uncertainty of each source count, $N_{S,i}$. So, the input estimates R_i will be treated as if they were uncorrelated, and the following equations will be used to calculate the combined standard uncertainty of ε:

$$u^2(\overline{R}) = s^2(\overline{R}) = \frac{1}{n(n-1)} \sum_{i=1}^{n} (R_i - \overline{R})^2$$

$$u_c(\varepsilon) = \sqrt{\frac{u^2(\overline{R})}{a_S^2} + \varepsilon^2 \frac{u^2(a_S)}{a_S^2}}$$

Assume the following data were obtained for the 15 calibration sources.

Source number, i	Uncorrected mass (g)	Buoyancy-corrected mass, m_i / g	Gross count, $N_{S,i}$	R_i / ($s^{-1} \cdot g^{-1}$)
1	1.0056	1.00663	18,375	60.832
2	1.0031	1.00413	18,664	61.943
3	1.0058	1.00683	18,954	62.737
4	1.0082	1.00924	19,249	63.562
5	1.0069	1.00793	19,011	62.857
6	1.0074	1.00843	18,936	62.578
7	1.0048	1.00583	18,537	61.417
8	1.0069	1.00794	18,733	61.937
9	1.0031	1.00413	18,812	62.434
10	1.0079	1.00894	18,546	61.258
11	1.0063	1.00734	18,810	62.229
12	1.0067	1.00774	19,273	63.736
13	1.0055	1.00653	18,893	62.554
14	1.0091	1.01014	18,803	62.033
15	1.0030	1.00403	18,280	60.674
			Average, $\overline{R}$ / ($s^{-1} \cdot g^{-1}$):	62.1854
			Experimental standard deviation, $s(R_i)$ / ($s^{-1} \cdot g^{-1}$):	0.8910
			Experimental standard deviation of the mean, $s(\overline{R})$ / ($s^{-1} \cdot g^{-1}$):	0.2301

Then the estimated counting efficiency is

$$\varepsilon = \frac{\overline{R}}{a_S} = \frac{62.1854\ s^{-1} \cdot g^{-1}}{150.0\ Bq/g} = 0.4146$$

and the (combined) standard uncertainty of ε is given by

$$u(\varepsilon) = \sqrt{\frac{(0.2301\ \mathrm{s^{-1}\cdot g^{-1}})^2}{(150.0\ \mathrm{Bq/g})^2} + 0.4146^2 \times \frac{(2.0\ \mathrm{Bq/g})^2}{(150.0\ \mathrm{Bq/g})^2}} = 0.005736$$

which may be rounded to 0.0057. (Note that the relative standard uncertainty of ε is approximately 1.4 %, which is large enough to justify neglecting the small uncertainties of the masses.)

In fact the standard uncertainty of ε calculated in the preceding example may be incomplete. The true counting efficiency may vary from source to source because of variations in geometry, position and other influence quantities not explicitly included in the model. So, the standard uncertainty of ε should include not only the standard uncertainty of the estimated mean, as calculated in the example, but also another component of uncertainty due to variations of the true efficiency during subsequent measurements. The additional component may be written as $\varepsilon\varphi$, where φ is the coefficient of variation of the true efficiency. Then the total uncertainty of ε is obtained by squaring the original uncertainty estimate, adding $\varepsilon^2\varphi^2$, and taking the square root of the sum.

$$u(\varepsilon) = \sqrt{\frac{u^2(\overline{R})}{a_S^2} + \varepsilon^2\left(\frac{u^2(a_S)}{a_S^2} + \varphi^2\right)} \tag{19.26}$$

In the example above, the experimental variance of the ratios, R_i, may be used to estimate φ. Section 18B.2 of Attachment 18B, describes an approach for estimating such "excess" variance in a series of measurements. When the methods of Section 18B.2 are used with these data, the resulting estimate of φ is approximately 0.012, or 1.2 %. So, the total uncertainty of ε as a predictor of the counting efficiency for a source prepared and counted at some time in the future is

$$u(\varepsilon) = \sqrt{\frac{(0.2301\ \mathrm{s^{-1}\cdot g^{-1}})^2}{(150.0\ \mathrm{Bq/g})^2} + 0.4146^2\left(\frac{(2.0\ \mathrm{Bq/g})^2}{(150.0\ \mathrm{Bq/g})^2} + 0.012^2\right)} = 0.0076 \tag{19.27}$$

Variations in counting efficiency due to source placement should be reduced as much as possible through the use of positioning devices that ensure a source with a given geometry is always placed in the same location relative to the detector. If such devices are not used, variations in source position may significantly increase the measurement uncertainty.

Calibrating an instrument under conditions different from the conditions under which test sources are counted may lead to large uncertainties in the sample activity measurements. Source geometry in particular tends to be an important factor for many types of radiation counters. Generally, calibration sources should be prepared with the sizes and shapes of test sources and counted in the same positions, although in some cases it may be possible to calculate correction factors which allow one calibration to be used for different geometries. When correction factors are used, their uncertainties should be evaluated and propagated.

If the efficiency, ε, is calculated from a model that includes one of the quantities X_i appearing elsewhere in the sample activity model, there is a correlation between the measured values of ε and X_i, which should not be ignored. It is often simpler to include the entire expression for ε in the expression for the laboratory sample activity before applying the uncertainty propagation formula.

EXAMPLE 19.21 Suppose the counting efficiency for a measurement is modeled by the equation $\varepsilon = A \exp(-B m_S)$, where A and B are calibration parameters and m_S is the source mass; and suppose the chemical yield Y is modeled by m_S / m_C, where m_C is the expected mass at 100 % recovery. Then the estimated values of the counting efficiency and the yield are correlated, because both are calculated from the same measured value of the source mass. When the combined standard uncertainty of the sample activity is calculated, the covariance $u(\varepsilon, Y)$ may be included in the uncertainty propagation formula (see Section 19.4.4), or the variables ε and Y in the model may be replaced by the expressions $A \exp(-B m_S)$ and m_S / m_C, respectively, before the sensitivity coefficients are calculated.

In some cases the estimated value of the counting efficiency has *no effect* on the output estimate of laboratory sample activity. This happens often in alpha-particle spectrometry, for example, when isotopic tracers are used. The efficiency estimate is needed to obtain an estimate of the yield of the chemistry procedure, but the efficiency usually cancels out of the mathematical model for the laboratory sample activity and its uncertainty is not propagated when determining the combined standard uncertainty of the activity estimate.

19.5.7 Radionuclide Half-Life

The component of combined standard uncertainty associated with the half-life of a radionuclide is often negligible in measurements performed by typical radioanalytical laboratories, since the half-lives of most radionuclides of interest have been measured very accurately and in many cases decay times are short relative to the half-life (so that the sensitivity coefficient is small). However, this uncertainty component is also one of the most easily obtained components, since radionuclide half-lives and their standard uncertainties are evaluated and published by the National Nuclear Data Center (NNDC) at Brookhaven National Laboratory. The data may be obtained from the NNDC web site (www.nndc.bnl.gov).

19.5.8 Gamma-Ray Spectrometry

Most radiochemistry laboratories rely on commercial software for the analysis of gamma-ray spectra and for the evaluation and propagation of the associated uncertainties. There are a number of sources of measurement uncertainty in gamma-ray spectrometry, including:

- Poisson counting uncertainty;
- Compton baseline determination;
- Background peak subtraction;
- Multiplets and interference corrections;
- Peak-fitting model errors;
- Efficiency calibration model error;
- Summing;
- Density-correction factors; and
- Dead time.

See Chapter 16 for further discussion of measurement models and uncertainty analysis for gamma-ray spectrometry, but note that neither Chapter 16 nor this chapter attempts to describe all of the relevant issues in detail.

19.5.9 Balances

The uncertainty of a balance measurement tends to be small, even negligible, when the balance is used properly and the mass being measured is much larger than the balance's readability. However, the uncertainty may also be difficult to evaluate unless the balance is well maintained and operated in a controlled environment that protects it from external influences. In particular, drafts or sudden changes in pressure, temperature or humidity (e.g., opening doors or dishwashers) may produce spurious errors.

Even if one assumes the balance measurement uncertainty is negligible, there are reasons for performing at least a partial evaluation of the uncertainty. One reason is to confirm the assumption that the uncertainty is negligible or to determine the range of measurement conditions under which the assumption is true. For example the uncertainty may be significant if the mass being weighed is comparable in magnitude to the readability of the balance, or if the mass is calculated as the difference between two much larger and nearly equal masses that are determined at different times and under possibly different environmental conditions (e.g., a planchet and filter weighed before and after adding a small amount of precipitate to the filter). Another reason is to establish acceptance criteria for the strict quality control necessary to ensure that the uncertainty remains negligible.

The uncertainty of a mass measurement generally has components associated with

- Calibration;
- Linearity;
- Repeatability;
- Day-to-day or hour-to-hour variability due to environmental factors; and
- Air buoyancy.

Other sources of uncertainty may include leveling errors and off-center errors, which should be controlled. Static electrical charges may also have an effect. For some materials gain or loss of mass before or after weighing (e.g., by absorption or evaporation of water) may be significant. Attachment 19E of this chapter describes balance measurement uncertainties in more detail.

Balance manufacturers provide specifications for repeatability and linearity, which are usually of the same order of magnitude as the balance's readability, but tests of repeatability and linearity should also be included in the routine quality control for the balance.

Repeatability is expressed as a standard deviation, s_r, and is typically assumed to be independent of the load. It represents the variability of the result of zeroing the balance, loading and centering a mass on the pan, and reading the final balance indication. Attachment 19E describes procedures for evaluating the repeatability experimentally.

The linearity tolerance of a balance, a_L, should be specified by the manufacturer as the maximum deviation of the balance indication from the value that would be obtained by linear interpolation between the calibration points. Different methods may be used to convert this tolerance to a standard uncertainty, depending on the form the linearity error is assumed to take. One method, which is recommended by the *Eurachem/CITAC Guide: Quantifying Uncertainty in Analytical Measurement*, is to treat the tolerance, a_L, as the half-width of a rectangular distribution and divide a_L by $\sqrt{3}$ to obtain the standard uncertainty (Eurachem, 2000). Another method, suggested in Attachment 19E of this chapter, is to treat the linearity error as a sinusoidal function of the load, with amplitude a_L. This model requires that a_L be divided by $\sqrt{2}$ to obtain the standard uncertainty. The latter method is used below.

Procedures for evaluating the relative standard uncertainties due to calibration and environmental factors and for calculating the buoyancy-correction factor and its standard uncertainty are described in Attachment 19E.

When one evaluates the uncertainty of a balance measurement that is performed as part of a typical radiochemical measurement, where the relative combined standard uncertainty of the final result is usually 5 % or more, often much more, the evaluation may involve only a few components of the uncertainty. Important components for this purpose include those due to repeatability, linearity, and environmental factors. Gains or losses of mass may be important in some cases, but calibration errors and buoyancy effects usually can be ignored, since they tend to be significant in the mass measurement only when the total uncertainty of the mass is so small

that it is negligible in the overall analytical process. The remainder of this section will consider only the mass uncertainties due to repeatability, linearity, and environmental factors (but see Attachment 19E).

A typical mass measurement in the laboratory involves separate measurements of a gross mass and a tare mass. The net mass, m, is determined by subtracting the balance indication for the tare mass, I_{tare}, from the indication for the gross mass, I_{gross}. That is,

$$m = I_{\text{net}} = I_{\text{gross}} - I_{\text{tare}} \tag{19.28}$$

If the tare and gross measurements are made under the same environmental conditions (e.g., at nearly the same time), the standard uncertainty of m is given (according to the simplified model) by

$$u(m) = \sqrt{2s_{\text{r}}^2 + a_{\text{L}}^2 + m^2\varphi_{\text{env}}^2} \tag{19.29}$$

where

m	is the net mass;
s_{r}	is the repeatability standard deviation;
a_{L}	is the linearity tolerance; and
φ_{env}	is the relative standard uncertainty due to environmental effects.

In some cases the balance is simply zeroed before adding the mass and there is no tare measurement. (Unfortunately the operation of zeroing the balance is often called "taring.") In such cases the factor 2 that appears before s_{r}^2 in Equation 19.29 should be omitted.

If tare and gross measurements are made under possibly different environmental conditions (e.g., on different days), then the following expression should be used to account for the greater uncertainty due to environmental effects.

$$u(m) = \sqrt{2s_{\text{r}}^2 + a_{\text{L}}^2 + \left(I_{\text{tare}}^2 + I_{\text{gross}}^2\right)\varphi_{\text{env}}^2} \tag{19.30}$$

EXAMPLE 19.22 The chemical yield (recovery) for a strontium analysis is determined gravimetrically by weighing a stainless steel planchet before and after evaporating a strontium nitrate solution onto it, and then dividing the net mass by the predicted mass of strontium nitrate at 100 % yield. The balance has readability 0.0001 g. According to the manufacturer it has repeatability 0.00010 g and linearity 0.00020 g, and these values have been reasonably well confirmed by historical QC data. The analyst has also used balance QC data to determine that the relative standard uncertainty due to environmental effects is approximately 2×10^{-5} (see Attachment 19E). Suppose for a particular measurement the tare mass of the planchet is 8.5923 g and the gross mass, which is measured two hours later, is 8.5978 g. Then the net mass is

$$m = 8.5978\ \text{g} - 8.5923\ \text{g} = 0.0055\ \text{g}$$

Since two hours elapse between the tare and gross measurements, Equation 19.30 is used to calculate the standard uncertainty.

$$\begin{aligned} u(m) &= \sqrt{2 s_r^2 + a_L^2 + \left(I_{tare}^2 + I_{gross}^2\right) \varphi_{env}^2} \\ &= \sqrt{2\,(0.00010\ \text{g})^2 + (0.00020\ \text{g})^2 + \left((8.5923\ \text{g})^2 + (8.5978\ \text{g})^2\right)(2 \times 10^{-5})^2} \\ &= 0.00035\ \text{g} \end{aligned}$$

Thus the relative standard uncertainty is approximately 6 %, which is significant in the determination of a yield factor.

Note that using the linearity tolerance, 0.00020 g, is rather conservative when the difference between the gross and tare masses is so small, but the uncertainty component due to linearity is not dominant in this example. It is actually smaller than the uncertainty due to environmental effects.

EXAMPLE 19.23 An aliquant of dry soil is subsampled for analysis and weighed on the same laboratory balance described in the preceding example. The repeatability of the balance is 0.00010 g, the linearity is 0.00020 g, and the relative standard uncertainty due to environmental effects is 2×10^{-5}. Suppose the analyst zeros the balance with an empty container on the pan, adds the aliquant of soil to the container, and reads the final balance indication without a significant time delay. If the final indication is 1.0247 g, then the mass estimate is m = 1.0247 g and its standard uncertainty is

$$\begin{aligned} u(m) &= \sqrt{s_r^2 + a_L^2 + m^2 \varphi_{Env}^2} \\ &= \sqrt{(0.00010\ \text{g})^2 + (0.00020\ \text{g})^2 + (1.0247\ \text{g})^2 (2 \times 10^{-5})^2} \\ &= 0.00022\ \text{g} \end{aligned}$$

So, the relative standard uncertainty is approximately 0.022 %, which is likely to be negligible in comparison to the uncertainty of subsampling (heterogeneity).

Note that in this example the uncertainty due to environmental effects is the smallest of the three uncertainty components.

19.5.10 Pipets and Other Volumetric Apparatus

Generally, a pipet or volumetric flask is used not to measure an existing volume of liquid, but to obtain a volume of a predetermined nominal size. The nominal value is treated as if it were a measured value, although it is known before the "measurement." The true volume is the variable quantity. Since a volumetric "measurement" of this type cannot be repeated, pipets and flasks are good examples of measurement systems for which historical data are important for Type A evaluations of standard uncertainty.

The uncertainty of a pipet measurement, like that of a balance measurement, is often relatively small in comparison to other uncertainties in a radiochemical analysis. However, the use of the wrong type of pipetting device for a particular measurement may result in a relatively large pipetting uncertainty. For example, one manufacturer's technical specifications for various models of pipetting devices list precision values that range from 0.1 % to 5 % and bias tolerances that range from 0.3 % to 12 %. (Here a "bias tolerance" means an upper bound for the possible magnitude of the pipet's unknown systematic error.) So, it is important for the user of a particular model to know its performance characteristics.

The total uncertainty of a volumetric measurement may include several components, but since most of the components are negligible in a typical radiochemical measurement process, a very simple method of evaluation is usually adequate as long as quality control is strict enough to ensure that the measuring devices and personnel are performing as expected. The method suggested here considers only two components, which are associated with precision and the capacity (or bias) of the device. Attachment 19E presents more complete methods of evaluation.

Any volumetric measuring device should have a specified tolerance for its capacity, or for the possible bias of the device (e.g., ASTM E288 and ASTM E969). This tolerance, δ_{cap}, may be assumed to represent the half-width of a rectangular or triangular distribution. Assuming a triangular distribution, as recommended by the Eurachem/CITAC Guide, one evaluates the uncertainty component of the volume associated with the capacity as $\delta_{cap} / \sqrt{6}$ (Eurachem, 2000).

The simplest type of uncertainty evaluation is possible when the manufacturer of a pipetting device provides specifications for both bias and precision (e.g., Eppendorf® pipettes). In this case the Type B standard uncertainty of a pipetted volume, V, may be evaluated as

$$u(V) = \sqrt{s^2 + \frac{\delta_{cap}^2}{6}} \tag{19.31}$$

where δ_{cap} is the manufacturer's stated bias tolerance and s is the stated standard deviation.

EXAMPLE 19.24 Suppose the manufacturer of a 5-milliliter pipetting device specifies the relative bias tolerance to be 0.6 % and the relative precision to be 0.2 %. Then the standard uncertainty of the volume may be evaluated as

$$u(V) = \sqrt{s^2 + \frac{\delta_{cap}^2}{6}} = \sqrt{(5\text{ mL} \times 0.002)^2 + \frac{(5\text{ mL} \times 0.006)^2}{6}} = 0.0158\text{ mL}$$

The relative standard uncertainty in this case is only about 0.3 %, which might be considered negligible for many applications.

EXAMPLE 19.25 Suppose the relative bias tolerance for an adjustable-volume pipetting device is 2.5 % when the device is set at 10 µL, and the relative precision is 0.7 %. Then the standard uncertainty of a volume delivered at the 10-microliter setting may be evaluated as

$$u(V) = \sqrt{s^2 + \frac{\delta_{cap}^2}{6}} = \sqrt{(10\text{ µL} \times 0.007)^2 + \frac{(10\text{ µL} \times 0.025)^2}{6}} = 0.124\text{ µL}$$

The relative standard uncertainty in this case is about 1.2 %, which would be considered potentially significant for many types of measurements.

When volumetric glassware is used, or when the manufacturer does not specify the precision, the uncertainty due to imprecision must be determined by other means. One Type B method of evaluating the imprecision for volumetric glassware is to examine the dimensions of the glassware and use experience and professional judgment to estimate the maximum possible deviation of the meniscus from the capacity line. If δ_{men} denotes this maximum deviation and d denotes the internal diameter of the glassware at the capacity mark, the maximum deviation of the volume from its value at the capacity mark is given by $\pi\delta_{men}d^2/4$. Note that if δ_{men} and d are expressed in centimeters, this expression gives a value in milliliters. Then, if δ_{men} is assumed to be the half-width of a triangular distribution, the standard uncertainty of V is given by the following equation

$$u(V) = \sqrt{\frac{\delta_{cap}^2 + (\pi\delta_{men}d^2/4)^2}{6}} \qquad (19.32)$$

A Type A (experimental) method of evaluation may also be used (see Attachment 19E).

EXAMPLE 19.26 Suppose the inside diameter of an ASTM Class-A 1-milliliter volumetric pipet is 0.4 cm, and the analyst estimates δ_{men}, the maximum deviation from the capacity line, to be 0.075 cm. The capacity tolerance, δ_{cap}, is specified by ASTM E969 to be 0.006 mL. So, the standard uncertainty of the volume (V = 1 mL) is

$$u(V) = \sqrt{\frac{\delta_{cap}^2 + (\pi \delta_{men} d^2 / 4)^2}{6}}$$

$$= \sqrt{\frac{(0.006\ \text{mL})^2 + (\pi\,(0.075\ \text{cm})(0.4\ \text{cm})^2 / 4)^2}{6}}$$

$$= 0.00456\ \text{mL}$$

The relative standard uncertainty is approximately 0.5 %.

19.5.11 Digital Displays and Rounding

If a measuring device, such as an analytical balance, has a digital display with resolution δ, the standard uncertainty of a measured value is at least $\delta / 2\sqrt{3}$. This uncertainty component exists even if the instrument is completely stable.

A similar Type B method may be used to evaluate the standard uncertainty due to computer roundoff error. When a value x is rounded to the nearest multiple of 10^n, the component of uncertainty generated by roundoff error is $10^n / 2\sqrt{3}$. When rounding is performed properly and x is printed with an adequate number of figures, this component of uncertainty should be negligible in comparison to the total uncertainty of x.

EXAMPLE 19.27 The readability of a digital balance is 0.1 g. Therefore, the minimum standard uncertainty of a measured mass is $0.1 / 2\sqrt{3}$ = 0.029 g.

EXAMPLE 19.28 A computer printout shows the result x of a measurement as

```
3.40E+01 +- 9.2E-02
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where the expanded uncertainty is calculated using a coverage factor of 2. Since the coverage factor is 2, the printout implies the standard uncertainty is 0.092 / 2, or 0.046. However, since the measured value is rounded to the nearest multiple of 0.1, the standard uncertainty of x should be increased from 0.046 to

$$u(x) = \sqrt{0.046^2 + \left(\frac{0.1}{2\sqrt{3}}\right)^2} = 0.054\,.$$

19.5.12 Subsampling

Appendix F of this manual discusses laboratory subsampling. The subsampling of heterogeneous materials for laboratory analysis increases the variability of the measurement result and thus adds a component of measurement uncertainty, which is usually difficult to quantify without replicate measurements. Appendix F summarizes important aspects of the statistical theory of particulate sampling and applies the theory to subsampling in the radiation laboratory (see also Gy, 1992, and Pitard, 1993). The mathematical estimates obtained using the theory often require unproven assumptions about the material analyzed and rough estimates of unmeasurable parameters. However, in some cases the theory can be used to suggest how subsampling errors may be affected by either changing the subsample size or grinding the material before subsampling. Of course the total measurement uncertainty, including components contributed by subsampling, may always be evaluated by repeated subsampling and analysis.

If subsampling is not repeated, its effects may be represented in the mathematical measurement model by including an input quantity F_S whose value is the ratio of the analyte concentration of the subsample to that of the total sample. This ratio, which will be called the *subsampling factor* (a MARLAP term), appears in the model as a divisor of the net instrument signal and thus is similar to the chemical yield, counting efficiency and other sensitivity factors. The value of F_S is estimated as 1, but the value has a standard uncertainty, $u(F_S)$, which increases the combined standard uncertainty of the result.

Although the component of uncertainty caused by the subsampling of heterogeneous solid matter may be difficult to estimate, it should not be ignored, since it may be relatively large and in some cases may even dominate all other components. One may use previous experience with similar materials to evaluate the uncertainty, possibly with the aid of the information and methods presented in Appendix F. Appendix F shows how the value of the subsampling uncertainty depends on the maximum particle diameter, d, the mass of the sample, m_L, and the mass of the subsample, m_S. The equation for the standard uncertainty of F_S typically has the form

$$u(F_S) = \sqrt{\left(\frac{1}{m_S} - \frac{1}{m_L}\right) k d^3} \qquad (19.33)$$

where the value of k depends on the sample. By default, if "hot particles" are not suspected, and if reasonable precautions are taken either to homogenize (mix) the material or to build the subsample from a large number of randomly selected increments, one may assume $k \approx 0.4$ g/cm^3, or

0.0004 g/mm^3. If hot particles are suspected, special measurement techniques are probably required, as described in Appendix F. In this case Equation 19.33 should not be used.

EXAMPLE 19.29

Problem: A 609-gram soil sample is ground until it passes through an ASTM #10 sieve, which has a mesh size of 2.0 mm. The sample is then homogenized and a 0.7957-gram subsample is removed. Use Equation 19.33 with $k = 0.0004$ g/mm^3 to evaluate the standard uncertainty of the subsampling factor, $u(F_S)$. Repeat the evaluation assuming an ASTM #18 sieve, whose mesh size is 1.0 mm.

Solution: First, assume $d = 2.0$ mm. Then the subsampling uncertainty is

$$u(F_S) = \sqrt{\left(\frac{1}{0.7957\ \text{g}} - \frac{1}{609\ \text{g}}\right)(0.0004\ \text{g/mm}^3)(2.0\ \text{mm})^3} = 0.063$$

Now assume $d = 1.0$ mm. Then

$$u(F_S) = \sqrt{\left(\frac{1}{0.7957\ \text{g}} - \frac{1}{609\ \text{g}}\right)(0.0004\ \text{g/mm}^3)(1.0\ \text{mm})^3} = 0.022$$

Another alternative is to evaluate the subsampling variance for each type of material and analyte at a specified maximum particle size, d, and subsample mass, m_S. Such an evaluation can be performed experimentally by repeated subsampling and analysis of one or more actual samples, provided that the concentrations are high enough and the measurement precision good enough to allow estimation of the variance attributable to subsampling. However, an artificially spiked sample is usually inappropriate for this purpose, because its heterogeneity differs from that of real samples. If the precision of the measurement process after subsampling is inadequate, the subsampling variance may be hard to quantify experimentally.

19.5.13 The Standard Uncertainty for a Hypothetical Measurement

MARLAP's recommended method selection criteria in Chapter 3 require that a laboratory estimate the standard uncertainty for a measurement of the activity concentration of a radionuclide in a hypothetical laboratory sample whose true concentration is specified (i.e., the "method uncertainty," as defined by MARLAP). To estimate the combined standard uncertainty of the measured concentration, one must obtain estimates for all the input quantities and their standard uncertainties. All quantities except the gross instrument signal may be measured and the standard uncertainties evaluated by routine Type A and Type B methods. Alternatively, the values and

their standard uncertainties may be determined from historical data. The estimate of the gross signal and its standard uncertainty must be obtained by other means, since the laboratory sample is only hypothetical. The predicted value of the gross count N_S is calculated by rearranging the equation or equations in the model and solving for N_S. The standard uncertainty of the measured value may then be evaluated either from theory (e.g., Poisson counting statistics), historical data, or experimentation.

EXAMPLE 19.30 Suppose the mathematical model for a radioactivity measurement is

$$a = \frac{N_S/t_S - N_B/t_B}{m_S Y \varepsilon e^{-\lambda(t_D + t_S/2)} F_S}$$

where

a	is the specific activity of the radionuclide in the sample;
N_S	is the test source count;
N_B	is the blank count;
t_S	is the source count time;
t_B	is the blank count time;
t_D	is the decay time;
m_S	is the mass of the test portion;
Y	is the chemical yield;
ε	is the counting efficiency;
λ	is the decay constant; and
F_S	is the subsampling factor.

With values given for the specific activity a; test portion mass m_S; blank count N_B; count times t_S, t_B, and t_D; efficiency ε; and yield Y; the source count N_S can be predicted. The predicted value is $N_S = t_S (a m_S Y \varepsilon \exp(-\lambda(t_D + t_S/2)) + N_B/t_B)$. When this value is treated like a measured value, its estimated variance according to Poisson statistics is $u^2(N_S) = N_S$. So, assuming negligible uncertainties in the times t_S, t_B, and t_D, the (first-order) uncertainty propagation formula gives the combined variance of the output estimate, a, as

$$u_c^2(a) = \frac{u^2(N_S)/t_S^2 + u^2(N_B)/t_B^2}{m_S^2 Y^2 \varepsilon^2 e^{-2\lambda(t_D + t_S/2)}} + a^2 \left(\frac{u^2(m_S)}{m_S^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(F_S)}{F_S^2} \right)$$

$$= \frac{(a m_S Y \varepsilon e^{-\lambda(t_D + t_S/2)} + N_B/t_B)/t_S + N_B/t_B^2}{m_S^2 Y^2 \varepsilon^2 e^{-2\lambda(t_D + t_S/2)}} + a^2 \left(\frac{u^2(m_S)}{m_S^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(F_S)}{F_S^2} \right)$$

19.6 References

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ATTACHMENT 19A
Statistical Concepts and Terms

19A.1 Basic Concepts

Every laboratory measurement involves a measurement error. Methods for analyzing measurement error are generally based on the theory of random variables. A *random variable* may be thought of as the numerical outcome of an experiment, such as a laboratory measurement, which produces varying results when repeated. In this document a random variable is most often the result of a measurement. Random variables will usually be denoted in this attachment by uppercase letters.

Of primary importance in almost any discussion of a random variable is its *distribution*, or *probability distribution*. The distribution of a random variable X describes the possible values of X and their probabilities. Although the word "distribution" has a precise meaning in probability theory, the term will be used loosely in this document. This attachment describes several types of distributions, including the following:

- normal (Gaussian)
- log-normal (or lognormal)
- chi-squared (or chi-square)
- Student's t
- rectangular (uniform)
- trapezoidal
- exponential
- binomial
- Poisson

Normal distributions are particularly important because they appear often in measurement processes. The other types listed are also important in this chapter, but only the exponential, binomial and Poisson distributions are described in the text.

The distribution of X is uniquely determined by its *distribution function*, defined by $F(x) = \Pr[X \le x]$, where $\Pr[X \le x]$ denotes the probability that X is less than or equal to x. The distribution function is also called the *cumulative distribution function* (cdf). If there is a function $f(x)$ such that the probability of any event $a \le X \le b$ is equal to $\int_a^b f(x)\,dx$ (i.e., the area under the curve $y = f(x)$ between $x = a$ and $x = b$), then X is a *continuous* random variable and $f(x)$ is a *probability density function* (pdf) for X. When X is continuous, the pdf uniquely describes its distribution. A plot of the pdf is the most often used graphical illustration of the distribution (e.g., see Figures 19.3 and 19.4), because the height of the graph over a point x indicates the probability that the value of X will be near x.

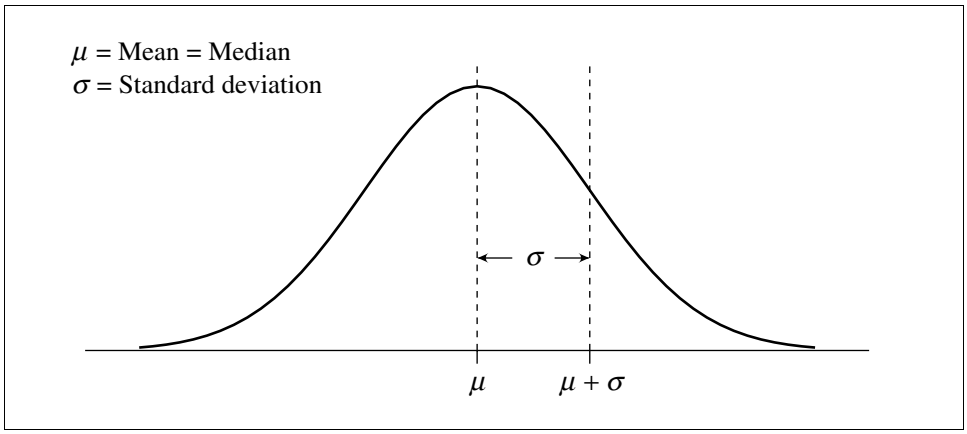

FIGURE 19.3 — A symmetric distribution

Two useful numerical characteristics of the distribution of a random variable are its *mean* and *variance*. The mean is also called the *expectation* or the *expected value* and may be denoted by μ_X or $E(X)$. The mean of a distribution is conceptually similar to the center of mass of a physical object. It is essentially a weighted average of all the possible values of X, where the weight of a value is determined by its probability. The variance of X, denoted by σ_X^2, Var(X), or $V(X)$, is a measure of the variability of X, or the dispersion of its values, and is defined as the expected value of $(X - \mu_X)^2$.

The *standard deviation* of X, denoted by σ_X is defined as the positive square root of the variance. Although the variance appears often in statistical formulas, the standard deviation is a more intuitive measure of dispersion. If X represents a physical quantity, then σ_X has the same physical dimension as X. The variance σ_X^2, on the other hand, has the dimension of X squared.

Any numerical characteristic of a distribution, such as the mean or standard deviation, may also be thought of as a characteristic of the random variables having that distribution.

The mean and standard deviation of a distribution may be estimated from a random sample of observations of the distribution. The estimates calculated from observed values are sometimes called the *sample mean* and *sample standard deviation*. Since the word "sample" here denotes a statistical sample of observations, not a physical sample in the laboratory, metrologists often use the terms *arithmetic mean, or average,* and *experimental standard deviation* to avoid confusion.

The mean is only one measure of the center of a distribution ("measure of central tendency"). Another is the median. The *median* of X is a value $x_{0.5}$ that splits the range of X into upper and lower portions which are equally likely, or, more correctly, a value $x_{0.5}$ such that the probability that $X \leq x_{0.5}$ and the probability that $X \geq x_{0.5}$ are both at least 0.5. Note that for some distributions the median may not be unique. Figure 19.4 shows the probability density function of a symmetric

distribution, whose mean and median coincide, and Figure 19.4 shows the pdf of an asymmetric distribution, whose mean and median are distinct.

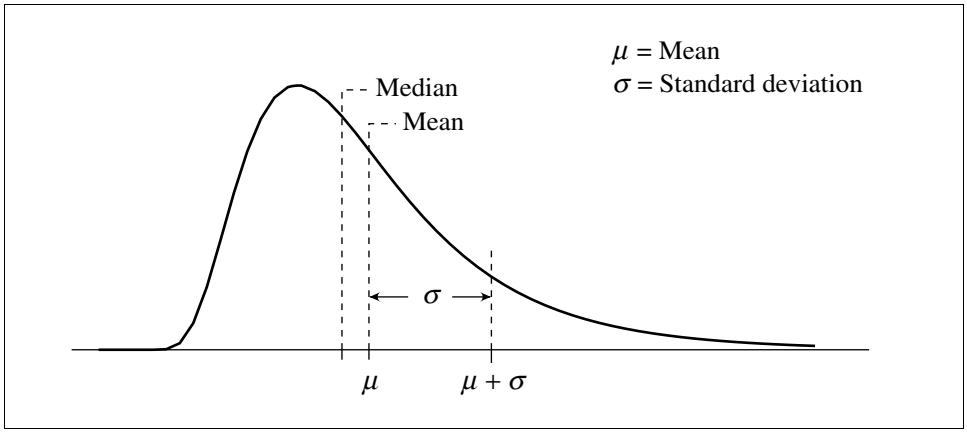

FIGURE 19.4 — An asymmetric distribution

The median of X is also called a *quantile of order* 0.5, or a 0.5-*quantile*. In general, if p is a number between 0 and 1, a p-quantile of X is a number x_p such that the probability that $X < x_p$ is at most p and the probability that $X \leq x_p$ is at least p. A p-quantile is often called a $100p^{\text{th}}$ *percentile*.

Sometimes the standard deviation of a nonnegative quantity is more meaningful when expressed as a fraction of the mean. The *coefficient of variation*, or CV, is defined for this reason as the standard deviation divided by the mean. The coefficient of variation is a dimensionless number, which may be converted to a percentage. The term "relative standard deviation," or RSD, is also used. The term "relative variance" is sometimes used to mean the square of the relative standard deviation.

The results of two analytical measurements may be *correlated* when they have measurement errors in common. This happens, for example, if laboratory samples are analyzed using the same instrument without repeating the instrument calibration. Any error in the calibration parameters affects all results obtained from the instrument. This type of association between two quantities X and Y is measured by their *covariance*, which is denoted by $\sigma_{X,Y}$ or $\text{Cov}(X,Y)$. The covariance of X and Y is defined as the expected value of the product $(X - \mu_X)(Y - \mu_Y)$.

Covariance, like variance, is somewhat nonintuitive because of its physical dimension. Furthermore, a large value for the covariance of two variables X and Y does not necessarily indicate a strong correlation between them. A measure of correlation must take into account not only the covariance $\sigma_{X,Y}$, but also the standard deviations σ_X and σ_Y. The *correlation coefficient*, denoted by $\rho_{X,Y}$, is therefore defined as $\sigma_{X,Y}$ divided by the product of σ_X and σ_Y. It is a dimensionless number between -1 and $+1$. The quantities X and Y are said to be strongly correlated when the absolute value of their correlation coefficient is close to 1.

Statistical formulas are generally simpler when expressed in terms of variances and covariances, but the results of statistical analyses of data are more easily understood when presented in terms of standard deviations and correlation coefficients.

The lack of a correlation between two quantities X and Y is not a sufficient condition to guarantee that two values $f(X)$ and $g(Y)$ calculated from them will also be uncorrelated. A stronger condition called *independence* is required. For most practical purposes, to say that two quantities are "independent" is to say that their random components are completely unrelated. A more rigorous definition appears in the MARLAP glossary.

When the value of a random variable X is used to estimate the value of an unknown parameter θ, then X is called an *estimator* for θ. The *bias* of X is the difference between the mean μ_X and the actual value θ. If the bias is zero, then X is said to be *unbiased*; otherwise, X is *biased*. Note that metrologists use the term "bias" with a somewhat different but similar meaning (see Section 19.3.1).

As mentioned in Section 19.4.5.2, even if X is an unbiased estimator for θ, the application of a nonlinear function, f, to X may produce a biased estimator, $f(X)$, for the value of $f(\theta)$. Colloquially speaking, the function of the mean is different from the mean of the function. For example, if X is an unbiased estimator for θ, then generally X^2 is a biased estimator for θ^2.

If the value of X is used not to estimate the value of a parameter but to "predict" the value of another random variable, Y, whose value oftentimes is not directly observed, then X is called a *predictor* for Y.

19A.2 Probability Distributions

This section briefly describes the probability distributions used in Chapter 19.

Distributions may be classified according to their mathematical properties. Distributions in the same class or family are described by the same mathematical formulas. The formulas involve numerical parameters which distinguish one member of the class from another.

Two important kinds of distributions are the normal and log-normal, which are observed often in nature. Other types of distributions important in radioanalysis include the rectangular, binomial, Poisson, Student's t, chi-squared and exponential distributions. Poisson distributions in particular are important in radiation counting measurements and are described in Section 19.5.2.

19A.2.1 Normal Distributions

Many quantities encountered in nature and in the laboratory have distributions which can be described by the "bell curve." This type of distribution, called a *normal*, or *Gaussian*, distribution, is usually a reasonably good model for the result of a radioanalytical measurement. A number of commonly used methods for evaluating data sets depend on their having an approximately normal distribution. The probability density function (pdf) for a normal distribution is shown in Figure 19.5.

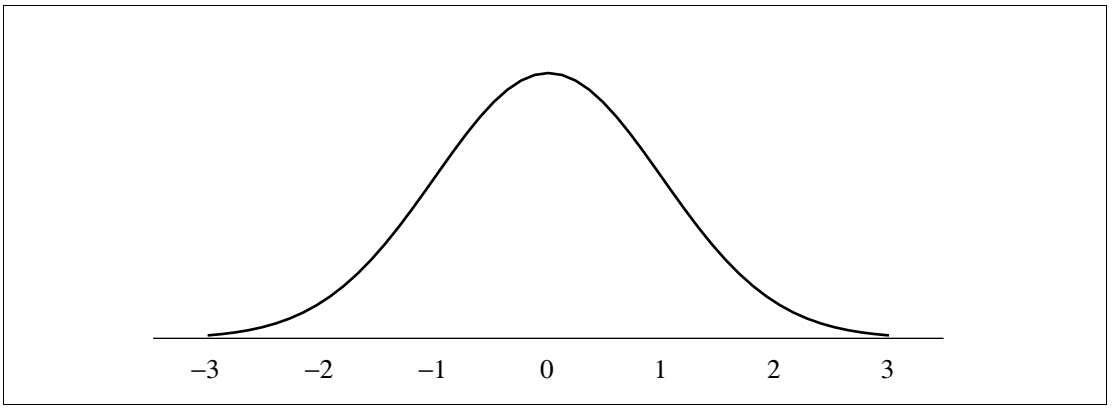

FIGURE 19.5 — A normal distribution

A normal distribution is uniquely specified by its mean μ and variance σ^2. The normal distribution with mean 0 and variance 1 is called the *standard normal distribution*. If X is normally distributed with mean μ and variance σ^2, then $(X - \mu) / \sigma$ has the standard normal distribution.

The sum of a large number of independent random variables has an approximately normal distribution, even if the individual variables themselves are not normally distributed, so long as the variance of each term is much smaller than the variance of the sum.[17] This is one reason why the normal distribution occurs often in nature. When a quantity is the result of additive processes involving many small random variations, the quantity tends to be normally distributed. It is also true that many other distributions, such as the binomial, Poisson, Student's *t* and chi-squared, can be approximated by normal distributions under certain conditions.

The mean value of a normal distribution is also its median, or the value that splits the range into equally likely portions.

[17] The number of quantities required to obtain a sum that is approximately normal depends on the distribution of the quantities. If the distribution is symmetric and mound-shaped like the bell curve, the number may be rather small. Other distributions such as the log-normal distribution, which is asymmetric, may require a much larger number.

The value of a normally distributed quantity will be within one standard deviation of the mean about 68 % of the time. It will be within two standard deviations about 95 % of the time and within three standard deviations more than 99 % of the time. It is important to remember that these percentages apply only to normal distributions.

19A.2.2 Log-normal Distributions

The concentration of a contaminant in the environment may not be normally distributed. Instead it often tends to be *log-normally* distributed, as shown in Figure 19.6.

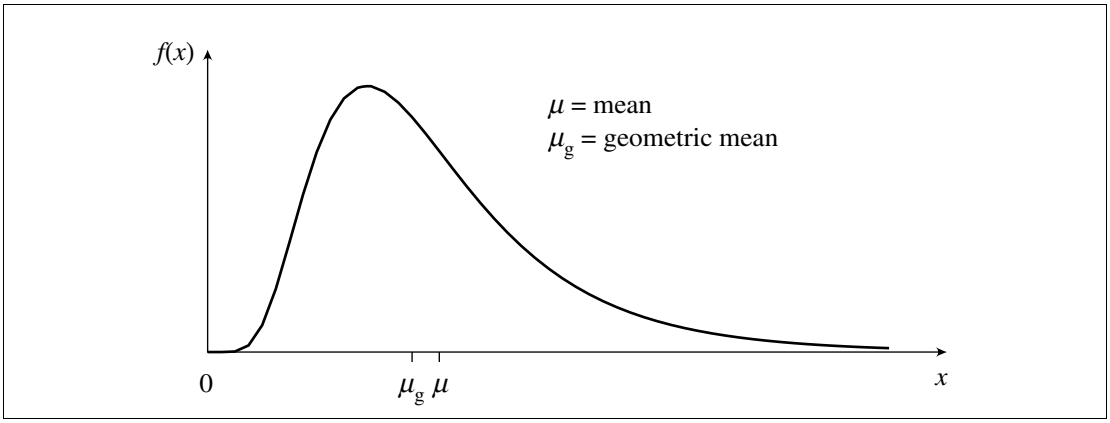

FIGURE 19.6 — A log-normal distribution

By definition, a quantity X has a log-normal (or lognormal) distribution if the logarithm of X is normally distributed. The product of a large number of independent positive random variables with similar variances is approximately log-normal, because the logarithm of the product is a sum of independent random variables, and the sum is approximately normal. The concentration of a contaminant in the environment tends to be log-normal because it is the result of processes of concentration and dilution, which are multiplicative.

The distribution of a log-normal quantity X can be uniquely specified by the mean $\mu_{\ln X}$ and variance $\sigma^2_{\ln X}$ of $\ln X$, but more commonly used parameters are the *geometric mean* $\mu_g = \exp(\mu_{\ln X})$ and the *geometric standard deviation* $\sigma_g = \exp(\sigma_{\ln X})$. The geometric mean and geometric standard deviation are defined so that, if k is a positive number, the probability that X will fall between μ_g / σ_g^k and $\mu_g \sigma_g^k$ is the same as the probability that $\ln X$, which is normally distributed, will fall between $\mu_{\ln X} - k\sigma_{\ln X}$ and $\mu_{\ln X} + k\sigma_{\ln X}$. For example, the value of X will be between μ_g / σ_g^2 and $\mu_g \sigma_g^2$ about 95 % of the time.

Although the mean and median of a normal distribution are identical, for a log-normal distribution these values are distinct. The median, in fact, is the same as the geometric mean μ_g. As shown in Figure 19.6, the mean μ is larger than the geometric mean μ_g . The mean may be cal-

culated from the geometric mean and geometric standard deviation as shown in Table G.6 in Appendix G.[18,19]

The log-normal distribution is important for the interpretation of environmental radiation data, but it may also have applications in the laboratory. Two possible applications are decay factors $e^{-\lambda t}$ based on uncertain time measurements and concentrations of contaminants in laboratory reagents.

19A.2.3 Chi-squared Distributions

If $Z_1, Z_2, \ldots, Z_\nu$ are independent random variables and each has the standard normal distribution, the sum $Z_1^2 + Z_2^2 + \cdots + Z_\nu^2$ has a *chi-squared* (or *chi-square*) *distribution with v degrees of freedom*. A chi-squared distribution, like a log-normal distribution, is asymmetric and does not include negative values. For large ν, the chi-squared distribution is approximately normal. Figure 19.7 shows the densities for chi-square distributions with 1, 2, 3 and 10 degrees of freedom.

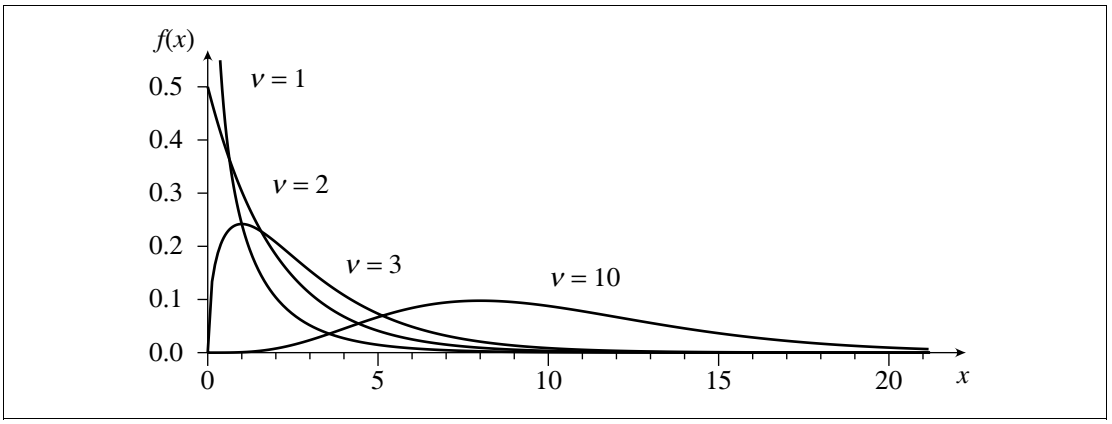

FIGURE 19.7 — Chi-squared distributions

Chi-squared distributions are used frequently in hypothesis testing, especially for tests of hypotheses about the variances of normally distributed data. Chi-squared distributions also appear in least-squares analysis (see Attachment 19C).

[18] Given the mean μ and standard deviation σ of the log-normal distribution, the geometric mean and geometric standard deviation may be calculated as $\mu_g = \mu^2 / \sqrt{\mu^2 + \sigma^2}$ and $\sigma_g = \exp\left(\sqrt{\ln(1 + \sigma^2 / \mu^2)}\right)$.

[19] Note that the symbols μ and σ are often used to denote the mean and standard deviation of ln X, which is normally distributed, rather than those of X, which is log-normally distributed.

A sum of independent chi-squared random variables is also chi-squared. Specifically, if X and Y are independent chi-squared random variables with ν_1 and ν_2 degrees of freedom, respectively, then $X + Y$ has a chi-squared distribution with $\nu_1 + \nu_2$ degrees of freedom.

The mean of a chi-squared distribution equals the number of degrees of freedom v, and the variance equals $2v$. The median does not have a simple formula.

19A.2.4 *T*-Distributions

If Z is standard normal, X is chi-squared with v degrees of freedom, and Z and X are independent, then $Z / \sqrt{X / v}$ has a *Student's t-distribution with v degrees of freedom*. A *t*-distribution is symmetric and mound-shaped like a normal distribution and includes both positive and negative values. Figure 19.8 shows the pdf for a *t*-distribution with 3 degrees of freedom. A dotted standard normal curve is also shown for comparison.

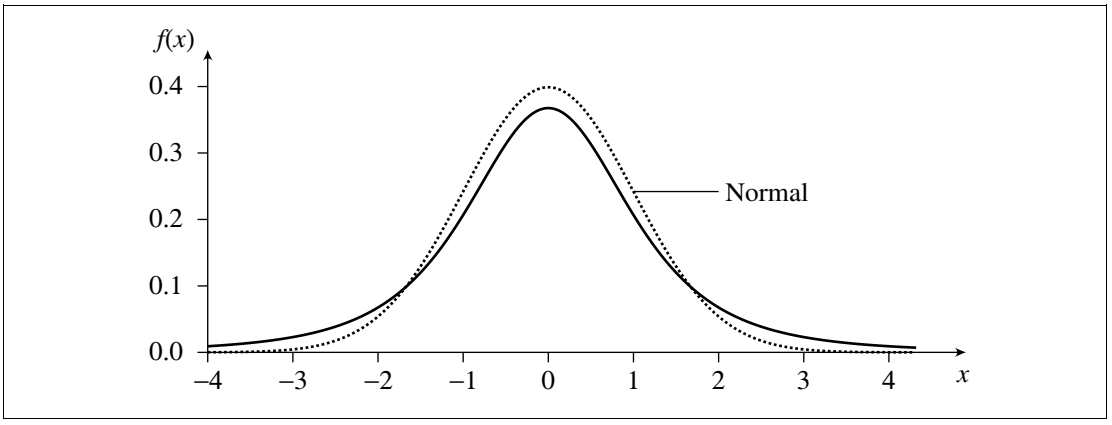

FIGURE 19.8 — The *t*-distribution with 3 degrees of freedom

When v is large, the *t*-distribution is virtually identical to the standard normal distribution.

The median of a *t*-distribution is zero. The mean is also zero if $v > 1$ but is undefined for $v = 1$. The variance equals $v / (v - 2)$ if $v > 2$ and is undefined otherwise.

T-distributions are often used in tests of hypotheses about the means of normally distributed data and are important in statistical quality control. *T*-distributions are also used in the procedure described in Attachment 19D for calculating measurement coverage factors.

If $X_1, X_2, \ldots, X_n$ are independent and normally distributed with the same mean μ and the same variance, then the quantity

$$\frac{\overline{X} - \mu}{s_X / \sqrt{n}}$$

where $\overline{X}$ is the arithmetic mean and s_X is the experimental standard deviation, has a *t*-distribution with $n - 1$ degrees of freedom.

If $X_1, X_2, \ldots, X_n, Y$ are independent and normally distributed with the same mean and variance, then the quantity

$$\frac{Y - \overline{X}}{s_X\sqrt{1 + 1/n}}$$

where $\overline{X}$ is the arithmetic mean of the X_i and s_X is the experimental standard deviation, has a *t*-distribution with $n - 1$ degrees of freedom.

If Z is standard normal, X is chi-squared with v degrees of freedom, Z and X are independent, and δ is a constant, then $(Z + \delta) / \sqrt{X / v}$ has the *noncentral t-distribution* with v degrees of freedom and noncentrality parameter δ (Stapleton, 1995). When the (central) *t*-distribution is used to test the null hypothesis that two normal distributions have the same mean, a noncentral *t*-distribution describes the distribution of the test statistic if the null hypothesis is false. For example, if $X_1, X_2, \ldots, X_n, Y$ are independent and normally distributed with the same variance σ^2, and $X_1, X_2, \ldots, X_n$ have the same mean μ_X, then the statistic

$$\frac{Y - \overline{X}}{s_X\sqrt{1 + 1/n}}$$

where $\overline{X}$ is the arithmetic mean of the X_i and s_X is the experimental standard deviation, has a *t*-distribution with $n - 1$ degrees of freedom if $\mu_X = \mu_Y$, but it has a noncentral *t*-distribution with noncentrality parameter

$$\delta = \frac{\mu_Y - \mu_X}{\sigma\sqrt{1 + 1/n}}$$

if $\mu_X \neq \mu_Y$.

The noncentral *t*-distribution is useful in the theory of detection limits and appears in Attachment 20A of Chapter 20, "Detection and Quantification Capabilities."

19A.2.5 Rectangular Distributions

If X only assumes values between a_- and a_+ and all such values are equally likely, the distribution of X is called a *rectangular distribution*, or a *uniform distribution* (see Figure 19.9).

The mean and median of the rectangular distribution equal the midrange $(a_- + a_+) / 2$, and the standard deviation is $(a_+ - a_-) / 2\sqrt{3}$.

Rectangular distributions are frequently used for Type B evaluations of standard uncertainty (see Sections 19.4.2.2 and 19.5.11).

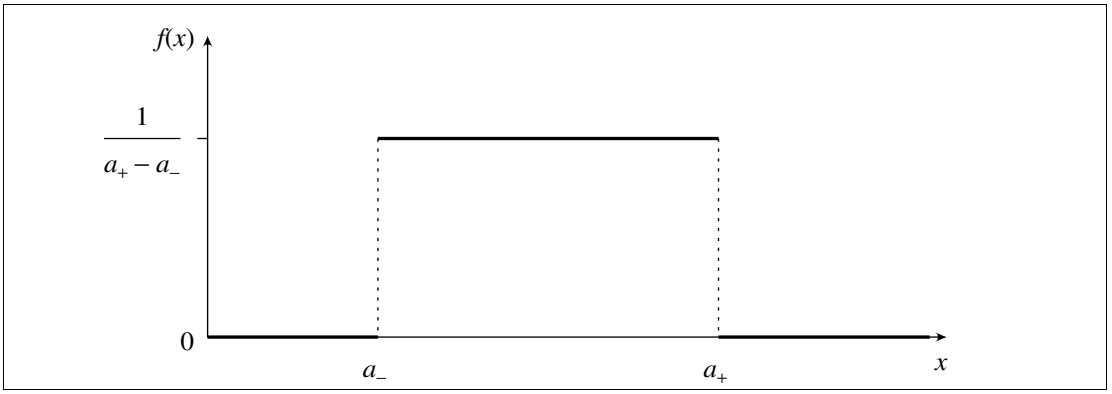

FIGURE 19.9 — A rectangular distribution

19A.2.6 Trapezoidal and Triangular Distributions

Another type of bounded distribution used for Type B evaluations of standard uncertainty is a *trapezoidal* distribution, which is described in Section 19.4.2.2. If X has a trapezoidal distribution, it only assumes values between two numbers a_- and a_+, but values near the midrange $(a_- + a_+) / 2$ are more likely than those near the extremes. The pdf for a symmetric trapezoidal distribution is shown in Figure 19.10. Asymmetric trapezoidal distributions are not considered here.

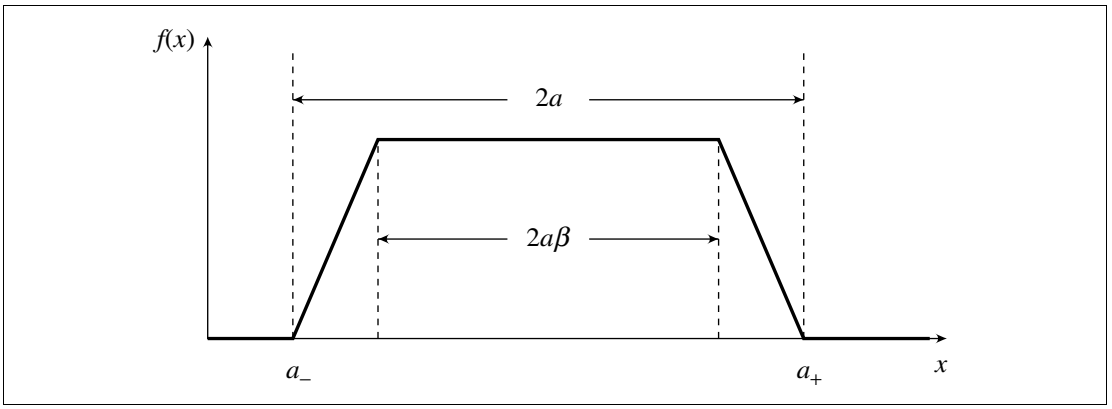

FIGURE 19.10 — A trapezoidal distribution

The mean and median of this distribution are both equal to the midrange. If the width of the trapezoid at its base is $2a$ and the width at the top is $2a\beta$, where $0 < \beta < 1$, then the standard deviation is $a\sqrt{(1 + \beta^2) / 6}$. As β approaches 0, the trapezoidal distribution approaches a *triangular distri-*

bution, whose standard deviation is $a / \sqrt{6}$, or $(a_+ - a_-) / 2\sqrt{6}$. As β approaches 1, the distribution approaches the rectangular distribution described in Section 19A.2.5.

19A.2.7 Exponential Distributions

The *exponential distribution* describes the life of an unstable atomic nucleus, whose remaining life does not depend on its current age. The distribution is described by one parameter, often denoted by λ, which represents the fractional decay rate. The mean of the distribution is $1 / \lambda$ and its variance is $1 / \lambda^2$. The median is the same as the half-life of the radionuclide. The pdf for an exponential distribution is shown in Figure 19.11.

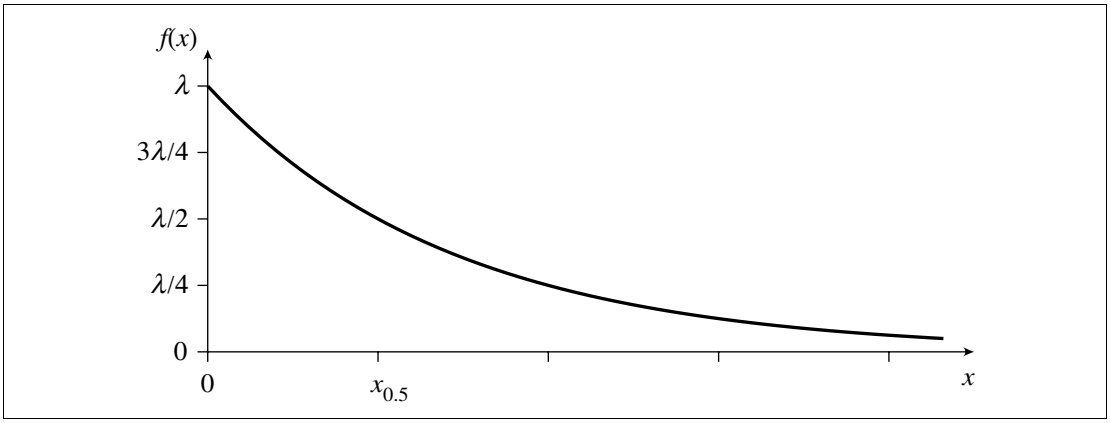

FIGURE 19.11 — An exponential distribution

The exponential distribution also describes waiting times between events in a Poisson process. For example, if the instrument background for a radiation counter follows the Poisson model with mean count rate r_B (see Section 19A.2.9), the waiting times between counts are exponentially distributed with parameter r_B.

19A.2.8 Binomial Distributions

The *binomial distribution*, introduced in Section 19.5.2, arises when one counts the outcomes of a series of n independent and identical experiments, each of which can produce the result "success" or "failure." If the probability of success for each event is p, the number of successes has a binomial distribution with parameters n and p. Important facts about the binomial distribution include the following:

- The distribution is discrete; its only possible values are 0, 1, 2, …, n.
- The mean of the distribution is np.
- The variance is $np(1 - p)$.
- If n is large and p is not close to 0 or 1, the distribution is approximated well by a normal distribution.

If X is binomial with parameters n and p, then for $k = 0, 1, 2, \ldots, n$, the probability that $X = k$ is given by the equation

$$\Pr[X = k] = \binom{n}{k} p^k (1-p)^{n-k} \tag{19.36}$$

where $\binom{n}{k}$ denotes a binomial coefficient, which equals $\frac{n!}{k!(n-k)!}$.

19A.2.9 Poisson Distributions

As explained in Section 19.5.2, the *Poisson distribution* arises naturally as an approximation to the binomial distribution when n is large and p is small. Even if n is not large, the variance of the binomial distribution can be approximated using the Poisson model if p is small. Other important facts about a Poisson distribution include the following:

- The distribution is discrete; its only possible values are the nonnegative integers 0, 1, 2, ….
- The mean and variance of the distribution are equal.
- If the mean is large, the distribution is well approximated by a normal distribution.
- A sum of independent Poisson random variables is also Poisson.

If X has a Poisson distribution with mean μ, then for any nonnegative integer n, the probability that $X = n$ is given by

$$\Pr[X = n] = \frac{\mu^n e^{-\mu}}{n!} \tag{19.37}$$

The Poisson distribution is related to the chi-squared distribution, since

$$\Pr[X \le n] = \Pr[\chi^2(2n + 2) \ge 2\mu] \qquad \text{and} \qquad \Pr[X \ge n] = \Pr[\chi^2(2n) \le 2\mu] \tag{19.38}$$

where $\chi^2(v)$ denotes a chi-squared random variable with v degrees of freedom. This fact allows one to use quantiles of a chi-squared distribution to construct a confidence interval for μ based on a single observation $X = n$ (Stapleton, 1995). Table 19.3 lists 95 % two-sided confidence intervals for μ some small values of n. For large values of n, the quantiles $\chi^2_p(2n)$ and $\chi^2_p(2n + 2)$ may be approximated using the Wilson-Hilferty formula (NBS, 1964):

$$\chi^2_p(v) \approx v\left(1 - \frac{2}{9v} + z_p\sqrt{\frac{2}{9v}}\right)^3 \tag{19.39}$$

As noted above, when the mean μ is large, the Poisson distribution may be approximated by a normal distribution. Specifically,

$$\Pr[X \le n] \approx \Phi\left(\frac{n + 0.5 - \mu}{\sqrt{\mu}}\right) \tag{19.40}$$

where Φ denotes the distribution function of the standard normal distribution. For most purposes, this approximation is adequate if $\mu \ge 20$.

Figures 19.12a and b show how the normal approximation improves as μ increases from 3 to 100. For any n, the probability $\Pr[X \le n]$ is represented by the total area of bars 0 to n, while the value given by the normal approximation is represented by the total area under the dotted curve to the left of the vertical line at $n + 0.5$.

TABLE 19.3 — 95 % confidence interval for a Poisson mean

n	$\mu_{\text{lower}} = \frac{1}{2}\chi^2_{0.025}(2n)$	$\mu_{\text{upper}} = \frac{1}{2}\chi^2_{0.975}(2n+2)$
0	0.000	3.689
1	0.025	5.572
2	0.242	7.225
3	0.619	8.767
4	1.090	10.242
5	1.623	11.668

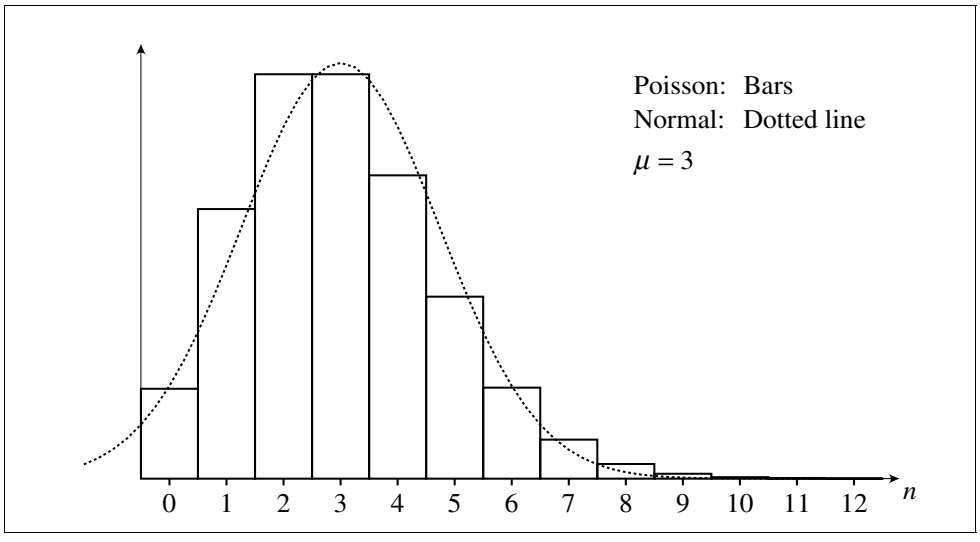

FIGURE 19.12a — Poisson distribution vs. normal distribution, $\mu = 3$

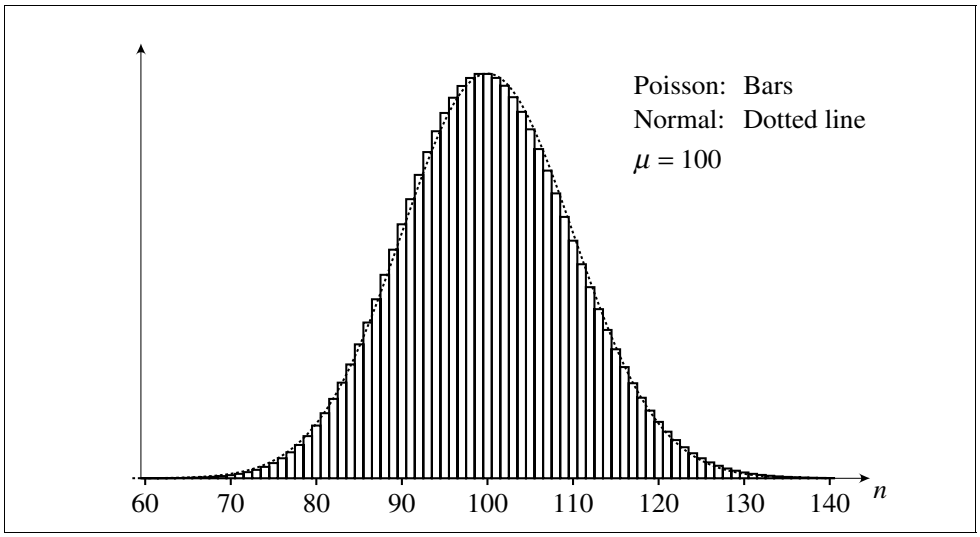

FIGURE 19.12b — Poisson distribution vs. normal distribution, $\mu = 100$

19A.3 References

National Bureau of Standards (NBS). 1964. *Handbook of Mathematical Functions*. Applied Mathematics Series 55, National Bureau of Standards, Gaithersburg, MD.

Stapleton, James H. 1995. *Linear Statistical Models*. John Wiley and Sons, New York, NY.

ATTACHMENT 19B
Example Calculations

19B.1 Overview

The following example shows how to calculate the combined standard uncertainty for a typical radioanalytical measurement.

19B.2 Sample Collection and Analysis

A soil sample is analyzed for $^{239/240}$Pu and ^{238}Pu by alpha-particle spectrometry.

- The sample is collected on July 10, 1999, at 11:17 am EDT, and shipped to a laboratory for analysis.

- The entire laboratory sample is dried, weighed and ground to a maximum particle size of 1.0 mm. The dry weight is approximately 2 kg.

- The prepared sample is homogenized, and a test portion is removed by increments. The documented procedure requires a test portion of approximately 0.5 g.

- The test portion is weighed and the mass is found to be 0.5017 g. The standard uncertainty of the mass includes contributions from repeatability, linearity, and sensitivity drift.

- A 1-milliliter aliquant of ^{242}Pu tracer is added to the test portion. The activity concentration of the tracer solution has previously been measured as 0.0705 Bq/mL with a standard uncertainty of 0.0020 Bq/mL on June 30, 1999, at 11:00 am CDT. The aliquant is dispensed by a pipet, whose dispensed volume has a combined standard uncertainty previously determined to be 0.0057 mL.

- After fusion, dissolution, chemical purification, and coprecipitation, a test source on a stainless steel planchet is prepared for counting in an alpha-particle spectrometer.

- The efficiency of the spectrometer for the chosen geometry, which is assumed to be independent of the particle energy, has previously been measured as 0.2805 with a standard uncertainty of 0.0045.

- A blank source is counted in the spectrometer for 60,000 s. The blank consists of a filter mounted on a planchet in the same geometry as the test source. In the ^{242}Pu region of interest, 2 counts are measured; and in the ^{238}Pu region of interest, 0 counts are measured. Historical

data for this and similar spectrometers at the laboratory indicate that the background is stable between measurements.

- The test source is placed in the spectrometer and counted for 60,000 s, beginning on August 24, 1999, at 4:47 pm CDT. In the ^{242}Pu region of interest, 967 counts are measured; and in the ^{238}Pu region of interest, 75 counts are measured.

- It is assumed that there is no detectable plutonium in the reagents; however, a method blank is analyzed simultaneously using a different spectrometer to check for contamination of reagents and glassware.

In this example the measurand will be the specific activity of ^{238}Pu in the 2-kilogram sample (dry weight) at the time of collection.

19B.3 The Measurement Model

The following notation will be used:

m_S	is the mass of the test portion (0.5017 g)
m_L	is the mass of the entire laboratory sample (~2000 g)
d	is the mesh size of the sieve (1.0 mm)
c_T	is the tracer activity concentration (0.0705 Bq/mL)
V_T	is the tracer aliquant volume (1 mL)
t_B	is the blank count time (60,000 s)
t_S	is the count time for the test source (60,000 s)
N_S	is the total count in a region of interest when the source is counted (^{238}Pu or ^{242}Pu)
N_B	is the count in a region of interest when the blank is counted (^{238}Pu or ^{242}Pu)
R	is the fraction of alpha particles with measured energy in the region of interest (^{238}Pu or ^{242}Pu)
D	is the decay-correction factor (^{238}Pu or ^{242}Pu)
ε	is the alpha-particle counting efficiency
Y	is the plutonium chemical yield fraction
F_S	is the subsampling factor (estimated as 1.00)
a_{238}	is the specific activity of ^{238}Pu in the dried laboratory sample, decay-corrected to the time of collection

Subscripts will be used to distinguish between quantities associated with particular regions of interest (^{238}Pu or ^{242}Pu).

The decay-correction factor for either isotope is calculated as follows:

$$D = \mathrm{e}^{-\lambda t_\mathrm{D}} \frac{1 - \mathrm{e}^{-\lambda t_\mathrm{S}}}{\lambda t_\mathrm{S}}$$

where λ is the decay constant (s^{-1}) and t_D is the time between collection and the start of the counting measurement (3,911,400 s). Since λt_S is small for both isotopes in this example, D may be approximated accurately by

$$D = \mathrm{e}^{-\lambda (t_\mathrm{D} + t_\mathrm{S}/2)}$$

The half-lives of ^{238}Pu and ^{242}Pu are 87.75 a and 375,800 a, respectively. So,

$$D_{238} = \exp\left(\frac{-\ln 2}{(87.75\ \mathrm{a}) \times (365.2422\ \mathrm{d/a}) \times (86{,}400\ \mathrm{s/d})} \left(3{,}911{,}400\ \mathrm{s} + \frac{60{,}000\ \mathrm{s}}{2} \right) \right)$$
$$= 0.9990$$

and $D_{242} = 1.000$.

Dead time is negligible in this example; so, no distinction is made between the real time and the live time. If the real time were greater than the live time, the correction for decay during the counting period would be based on the real time.

The fraction of alpha particles of each isotope actually measured in the nominal region of interest is estimated to lie between 0.96 and 1.00. A rectangular distribution is assumed, with center at 0.98 and half-width equal to 0.02. Then the Type B standard uncertainties of R_{238} and R_{242} are

$$u(R_{238}) = u(R_{242}) = \frac{0.02}{\sqrt{3}} = 0.01155$$

The chemical yield of plutonium is calculated using the model

$$Y = \frac{N_{\mathrm{S},242} / t_\mathrm{S} - N_{\mathrm{B},242} / t_\mathrm{B}}{c_\mathrm{T} V_\mathrm{T} \varepsilon R_{242} D_{242}}$$

Then the following model is used to estimate the measurand.

$$a_{238} = \frac{N_{\mathrm{S},238} / t_\mathrm{S} - N_{\mathrm{B},238} / t_\mathrm{B}}{m_\mathrm{S} Y \varepsilon R_{238} D_{238} F_\mathrm{S}}$$

When values are inserted,

$$Y = \frac{967 / (60{,}000 \text{ s}) - 2 / (60{,}000 \text{ s})}{(0.0705 \text{ Bq/mL}) \times (1 \text{ mL}) \times 0.2805 \times 0.98 \times 1} = 0.82990$$

$$a_{238} = \frac{75 / (60{,}000 \text{ s}) - 0 / (60{,}000 \text{ s})}{(0.5017 \text{ g}) \times 0.82990 \times 0.2805 \times 0.98 \times 0.9990 \times 1.00} = 0.010932 \text{ Bq/g}$$

(or 10.932 Bq/kg)

19B.4 The Combined Standard Uncertainty

The efficiency, ε, effectively cancels out of the equation for a_{238}, because it is multiplied by the yield Y and also appears as a factor in the denominator of the expression for Y (see also Section 19.5.6). Therefore, the uncertainty of ε has no effect on the uncertainty of a_{238}. When using the uncertainty propagation formula to calculate the combined standard uncertainty of a_{238}, one might include a covariance term for $u(Y, \varepsilon)$ to account for the relationship between the measured values of Y and ε, but it is simpler to treat $Y\varepsilon$ as one variable. Application of the first-order uncertainty propagation formula (Section 19.4.3) to the equations above then gives the following:

$$u_c^2(Y\varepsilon) = \frac{u^2(N_{S,242}) / t_S^2 + u^2(N_{B,242}) / t_B^2}{c_T^2 V_T^2 R_{242}^2 D_{242}^2} + (Y\varepsilon)^2 \left(\frac{u^2(c_T)}{c_T^2} + \frac{u^2(V_T)}{V_T^2} + \frac{u^2(R_{242})}{R_{242}^2} \right)$$

$$u_c^2(a_{238}) = \frac{u^2(N_{S,238}) / t_S^2 + u^2(N_{B,238}) / t_B^2}{m_S^2 (Y\varepsilon)^2 R_{238}^2 D_{238}^2} + a_{238}^2 \left(\frac{u^2(m_S)}{m_S^2} + \frac{u^2(Y\varepsilon)}{(Y\varepsilon)^2} + \frac{u^2(R_{238})}{R_{238}^2} + \frac{u^2(F_S)}{F_S^2} \right)$$

All other input estimates are assumed to be uncorrelated.

Note that $u^2(F_S)$ is the subsampling variance associated with taking a small test portion (0.5017 g) from a much larger sample (2000 g). The estimation method suggested in Section 19.5.12 will be used here to evaluate $u(F_S)$.

$$u(F_S) = \sqrt{\left(\frac{1}{m_S} - \frac{1}{m_L} \right) k d^3} \qquad \text{where } k = 0.0004 \text{ g/mm}^3$$

$$= \sqrt{\left(\frac{1}{0.5017 \text{ g}} - \frac{1}{2000 \text{ g}} \right) (0.0004 \text{ g/mm}^3)(1.0 \text{ mm})^3}$$

$$= 0.0282 .$$

Appendix F provides more information about subsampling errors and methods for estimating their variances.

The standard uncertainty of the mass of the test portion, m_S, is evaluated using the methods described in Section 19.5.9. The total uncertainty of m_S has components due to repeatability, linearity, and sensitivity drift (environmental factors). Assume the repeatability standard deviation is 0.0001 g, the linearity tolerance is 0.0002 g, and the relative standard uncertainty due to sensitivity drift is 1×10^{-5}. If the balance is zeroed with an empty container on the pan, the soil is added to the container, and the display is read, then the standard uncertainty of the mass m_S is

$$u(m_S) = \sqrt{(0.0001\text{ g})^2 + (0.0002\text{ g})^2 + (0.5017\text{ g})^2(1 \times 10^{-5})^2} = 2.2 \times 10^{-4}\text{ g}$$

Since extremely low counts are possible, each Poisson counting variance in this example will be estimated by the number of observed counts plus one (see Section 19.5.2.2 and Section 19D.3 of Attachment 19D). So, for example, $u(N_{B,238})$ equals one, not zero.

Table 19.4 summarizes the input estimates and their standard uncertainties.

TABLE 19.4 — Input estimates and standard uncertainties

INPUT QUANTITY	INPUT ESTIMATE	STANDARD UNCERTAINTY	MEASUREMENT UNIT	TYPE OF EVALUATION
m_S	0.5017	2.2×10^{-4}	g	Combined*
c_T	0.0705	0.0020	Bq/mL	Combined*
V_T	1.0000	0.0057	mL	Combined*
t_B	60,000	Negligible	s	B
t_S	60,000	Negligible	s	B
$N_{B,238}$	0	1	counts	B
$N_{B,242}$	2	1.73	counts	B
$N_{S,238}$	75	8.72	counts	B
$N_{S,242}$	967	31.1	counts	B
R_{238}, R_{242}	0.98	0.01155	none	B
ε	0.2805	0.0045	none	Combined*
F_S	1.00	0.0282	none	B
D_{238}	0.9990	Negligible	none	B
D_{242}	1.0000	Negligible	none	B

* "Combined" here means "determined by uncertainty propagation."

Other possible sources of uncertainty in alpha-particle spectrometry measurements include:

- uncertainties in half-lives and decay times;
- spillover and baseline interferences caused by poor peak resolution;
- incomplete equilibration of tracer and analyte before chemical separation; and
- changing instrument background.

These uncertainties are evaluated as negligible in this example. Uncertainties associated with half-lives and decay times are negligible, because the decay times in the example are much shorter than the half-lives; but in practice one should confirm that any other uncertainties are small enough to be neglected.

When values are inserted into the formulas

$$u_c^2(Y\varepsilon) = \frac{968 / (60{,}000\ \text{s})^2 + 3 / (60{,}000\ \text{s})^2}{(0.0705\ \text{Bq/mL})^2 \times (1\ \text{mL})^2 \times 0.98^2 \times 1^2} + (0.82990 \times 0.2805)^2 \left(\frac{0.0020^2}{0.0705^2} + \frac{0.0057^2}{1^2} + \frac{0.01155^2}{0.98^2} \right)$$

$$= 0.0001094007$$

$$= 0.01046^2$$

and

$$u_c^2(a_{238}) = \frac{76 / (60{,}000\ \text{s})^2 + 1 / (60{,}000\ \text{s})^2}{(0.5017\ \text{g})^2 \times (0.82990 \times 0.2805)^2 \times 0.98^2 \times 0.9990^2} + (0.010932\ \text{Bq/g})^2 \left(\frac{(2.2 \times 10^{-4})^2}{0.5017^2} + \frac{0.01046^2}{(0.82990 \times 0.2805)^2} + \frac{0.01155^2}{0.98^2} + \frac{0.0282^2}{1^2} \right)$$

$$= 1.98915 \times 10^{-6}\ \text{Bq}^2/\text{g}^2$$

$$= (0.001410\ \text{Bq/g})^2$$

So, $u_c(a_{238}) = 0.00141\ \text{Bq/g}$ or $1.41\ \text{Bq/kg}$. If the result is to be reported with an expanded uncertainty calculated from the combined standard uncertainty $u_c(a_{238})$ and a coverage factor $k = 2$, the result should appear as $(0.0109 \pm 0.0028)\ \text{Bq/g}$ or $(10.9 \pm 2.8)\ \text{Bq/kg}$ (dry weight).

ATTACHMENT 19C
Multicomponent Measurement Models

19C.1 Introduction

In this attachment, the term "multicomponent measurement model" means a mathematical model with more than one output quantity calculated from the same set of input quantities. One common application of a multicomponent model is the determination of a calibration curve involving two or more parameters. In principle, the approach to uncertainty propagation described in Section 19.4 applies equally well to single-component or multicomponent models. However, a straightforward implementation of the uncertainty propagation formula for some multicomponent models may be tedious unless software for automatic uncertainty propagation is available.

At the time of this writing, the joint working group responsible for the *GUM* is reported to be developing additional guidance to deal with multicomponent models, but the guidance is not yet available.

19C.2 The Covariance Matrix

A multicomponent model is most naturally described in terms of vectors and matrices, and the remainder of this attachment assumes the reader is familiar with those concepts and with the notation commonly used to describe them. The single-component model, $Y = f(X_1, X_2, \ldots, X_N)$, which was used earlier, is now replaced by a multicomponent model, $\boldsymbol{Y} = \boldsymbol{f}(\boldsymbol{X})$, where $\boldsymbol{X}$ and $\boldsymbol{Y}$ denote column vectors and $\boldsymbol{f}$ denotes a vector-valued function of $\boldsymbol{X}$. The input vector, which is formed from the input estimates, x_j, will be denoted by $\boldsymbol{x}$, and the output vector, which is formed from the output estimates, y_i, will be denoted by $\boldsymbol{y}$. The estimated variances and covariances of all the input estimates are arranged in a square matrix, called the *covariance matrix* and denoted here by $\boldsymbol{u}^2(\boldsymbol{x})$, whose ij^{th} element equals the covariance $u(x_i, x_j)$. Application of the covariance equation in Section 19.4.4 leads to the following expression for the covariance matrix of the output vector, $\boldsymbol{y}$.

$$\boldsymbol{u}^2(\boldsymbol{y}) = \left(\frac{\partial \boldsymbol{f}}{\partial \boldsymbol{x}} \right) \boldsymbol{u}^2(\boldsymbol{x}) \left(\frac{\partial \boldsymbol{f}}{\partial \boldsymbol{x}} \right)' \qquad (19.46)$$

In this equation, $\partial \boldsymbol{f} / \partial \boldsymbol{x}$ denotes the matrix whose ij^{th} element is $\partial f_i / \partial x_j$.

19C.3 Least-Squares Regression

One application for which specialized multicomponent methods for uncertainty propagation may be useful is least-squares regression. For example the method of least squares may be used to find an approximate solution, $\hat{\boldsymbol{y}}$, of a matrix equation of the form

$$\boldsymbol{A}\boldsymbol{y} \cong \boldsymbol{b} \tag{19.47}$$

where the components of the vector $\boldsymbol{b}$ have uncertainties. The least-squares solution for this problem can usually be expressed as

$$\hat{\boldsymbol{y}} = (\boldsymbol{A}'\boldsymbol{W}\boldsymbol{A})^{-1}\boldsymbol{A}'\boldsymbol{W}\boldsymbol{b} \tag{19.48}$$

where $\boldsymbol{W}$ denotes a diagonal weight matrix, whose i^{th} diagonal element is the inverse of the variance of b_i. If there is no uncertainty in the matrix $\boldsymbol{A}$, and the elements of $\boldsymbol{b}$ are uncorrelated, then the covariance matrix for $\hat{\boldsymbol{y}}$ is given simply by

$$\boldsymbol{u}^2(\hat{\boldsymbol{y}}) = (\boldsymbol{A}'\boldsymbol{W}\boldsymbol{A})^{-1} \tag{19.49}$$

If there are uncertainties in the elements of $\boldsymbol{A}$, the expression above is incomplete. Suppose the elements of $\boldsymbol{A}$ are functions of variables $z_1, z_2, \ldots, z_r$, whose estimated variances and covariances are available. Arrange these variables, z_j, in a column vector, $\boldsymbol{z}$, and let $\boldsymbol{u}^2(\boldsymbol{z})$ denote the covariance matrix. If the b_i are not correlated with the z_j, then a more complete expression for the covariance matrix of $\hat{\boldsymbol{y}}$ is the following.

$$\boldsymbol{u}^2(\hat{\boldsymbol{y}}) = (\boldsymbol{A}'\boldsymbol{W}\boldsymbol{A})^{-1} + \left(\frac{\partial \hat{\boldsymbol{y}}}{\partial \boldsymbol{z}}\right) \boldsymbol{u}^2(\boldsymbol{z}) \left(\frac{\partial \hat{\boldsymbol{y}}}{\partial \boldsymbol{z}}\right)' \tag{19.50}$$

The derivative matrix, $\partial\hat{\boldsymbol{y}} / \partial\boldsymbol{z}$, which appears above, may be calculated column by column. The j^{th} column of $\partial\hat{\boldsymbol{y}} / \partial\boldsymbol{z}$ is given by the formula

$$\frac{\partial \hat{\boldsymbol{y}}}{\partial z_j} = (\boldsymbol{A}'\boldsymbol{W}\boldsymbol{A})^{-1}\left(\frac{\partial \boldsymbol{A}'}{\partial z_j}\boldsymbol{W}(\boldsymbol{b} - \boldsymbol{A}\hat{\boldsymbol{y}}) - \boldsymbol{A}'\boldsymbol{W}\frac{\partial \boldsymbol{A}}{\partial z_j}\hat{\boldsymbol{y}}\right) \tag{19.51}$$

where $\partial\boldsymbol{A} / \partial z_j$ denotes the matrix obtained from $\boldsymbol{A}$ by differentiating each element with respect to z_j. If the uncertainties in the matrix $\boldsymbol{A}$ are large, even this method of uncertainty propagation may be inadequate (e.g., see Fuller, 1987).

19C.4 References

Fuller, Wayne A. 1987. *Measurement Error Models*. John Wiley and Sons, New York, NY.

International Organization for Standardization (ISO). 1995. *Guide to the Expression of Uncertainty in Measurement*. ISO, Geneva, Switzerland.

ATTACHMENT 19D
Estimation of Coverage Factors

19D.1 Introduction

Although it is common for laboratories to use a fixed coverage factor such as 2 or 3 when determining an expanded uncertainty for a measured value, the true coverage probability for the resulting interval may be lower than expected if the standard uncertainties of the input estimates are determined from evaluations with too few degrees of freedom. This attachment summarizes a general method presented in Annex G of the *GUM* for determining appropriate coverage factors in these circumstances (ISO, 1995). Section 19D.3 applies the method to Poisson counting uncertainties.

19D.2 Procedure

19D.2.1 Basis of Procedure

When one evaluates a parameter, θ, statistically by making a series of n independent, unbiased measurements under the same measurement conditions and averaging the results, x_i, if the results are approximately normally distributed, a confidence interval for θ may be constructed using the fact that the quantity $(\bar{x} - \theta) / s(\bar{x})$ has a t-distribution with $\nu = n - 1$ degrees of freedom. If the desired confidence level is p, then the confidence interval is $\bar{x} \pm t\,s(\bar{x})$, where $t = t_{(1+p)/2}(\nu)$ is the $(1 + p) / 2$-quantile of a t-distribution with ν degrees of freedom. Here, $\bar{x}$ is the result of the measurement of θ, and $s(\bar{x})$ is its standard uncertainty (Type A). The quantile, t, is the coverage factor that makes the coverage probability equal to p. For smaller values of ν, larger values of t are necessary to give the same coverage probability, because of the increased variability of the variance estimator, $s^2(\bar{x})$.

The procedure described below is derived by assuming that the output estimate, y, for a more complex measurement and the combined standard uncertainty, $u_c(y)$, can take the place of $\bar{x}$ and $s(\bar{x})$, respectively, in the confidence interval above; and that the appropriate coverage factor, k_p, can be approximated by a quantile of a t-distribution with an appropriate number of degrees of freedom. The number of degrees of freedom is determined from the estimated coefficient of variation of the variance estimator, $u_c^2(y)$.

19D.2.2 Assumptions

Assume the mathematical model for a measurement is $Y = f(X_1, X_2, \ldots, X_N)$, the input estimates $x_1, x_2, \ldots, x_N$ are independent, and the output estimate is $y = f(x_1, x_2, \ldots, x_N)$. Also assume that the combined standard uncertainty of y is not dominated by one component determined from a Type A evaluation with only a few degrees of freedom or from a Type B evaluation based on a distri-

bution very different from a normal distribution. Then the distribution of the output estimate y should be approximately normal, and the following procedure may be used to obtain a coverage factor, k_p, for the expanded uncertainty of y that gives a desired coverage probability, p.

19D.2.3 Effective Degrees of Freedom

First compute the *effective degrees of freedom* of the measurement, ν_{eff}, using the *Welch-Satterthwaite* formula

$$\frac{u_c^4(y)}{\nu_{\text{eff}}} = \sum_{i=1}^{N} \frac{u_i^4(y)}{\nu_i} \qquad \text{or} \qquad \nu_{\text{eff}} = \frac{u_c^4(y)}{\sum_{i=1}^{N} \frac{u_i^4(y)}{\nu_i}} \tag{19.52}$$

Here $u_i(y) = |\partial f / \partial x_i| \, u(x_i)$ is the component of the combined standard uncertainty generated by $u(x_i)$. If $u(x_i)$ is evaluated by a Type A method, then ν_i is the number of degrees of freedom for that evaluation. If $u(x_i)$ is evaluated instead by a Type B method, then ν_i may be defined as

$$\nu_i = \frac{1}{2} \frac{u^2(x_i)}{\sigma^2(u(x_i))} = \frac{1}{2} \left(\frac{\Delta u(x_i)}{u(x_i)} \right)^{-2} \tag{19.53}$$

where $\Delta u(x_i)$ is the estimated standard deviation of the standard uncertainty, $u(x_i)$, and $\sigma^2(u(x_i))$ denotes its square. This definition of ν_i for a Type B evaluation is an approximation based on the relationship between the number of degrees of freedom for a Type A evaluation and the coefficient of variation of the uncertainty estimator. In most cases estimation of $\Delta u(x_i)$ is subjective and requires professional judgment.[20]

In some cases one may consider the value of $\Delta u(x_i)$ for a Type B standard uncertainty to be zero or negligible, as for example when evaluating the uncertainty associated with rounding a number (Section 19.5.11) or when the standard uncertainty estimate, $u(x_i)$, is very conservative. In such cases one may assume $\nu_i = \infty$; so, the i^{th} term of the sum appearing in the denominator of the Welch-Satterthwaite formula vanishes.

If an input estimate, x_i, and its standard uncertainty, $u(x_i)$, are taken from a calibration certificate, the effective degrees of freedom for $u(x_i)$ may be stated on the certificate. In this case the stated number of degrees of freedom should be used as ν_i.

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[20] A more rigorously derived mathematical definition of ν_i in terms of $\Delta u(x_i)$ exists, but its use is not warranted given the usually subjective nature of the estimate of $\Delta u(x_i)$ and the other approximations involved in the Welch-Satterthwaite formula.

The number of effective degrees of freedom, ν_{eff}, satisfies the following inequalities.

$$\min_{1 \le i \le n} \nu_i \le \nu_{\text{eff}} \le \sum_{i=1}^{n} \nu_i \tag{19.54}$$

So, ν_{eff} is no worse than the worst value of ν_i and no better than the sum of all the ν_i. The maximum (best) value for ν_{eff} in Equation 19.54 is attained only if each ν_i is proportional to $u_i^2(y)$. This fact suggests that, at least for Type A uncertainty components, the fraction of the total uncertainty evaluation effort spent on a particular component, $u_i(y)$, should be based on the anticipated magnitude of $u_i^2(y)$.

19D.2.4 Coverage Factor

The coverage factor, k_p, is defined to be the $(1 + p) / 2$-quantile, $t_{(1+p)/2}(\nu_{\text{eff}})$, of a t-distribution with ν_{eff} degrees of freedom.[21] Since the calculated value of ν_{eff} will generally not be an integer, it must be truncated to an integer, or else an interpolated t-factor should be used. That is, if $n < \nu_{\text{eff}} < n + 1$, then use either $k_p = t_{(1+p)/2}(\lfloor \nu_{\text{eff}} \rfloor)$, where $\lfloor \cdot \rfloor$ denotes the truncation operator, or

$$k_p = (n + 1 - \nu_{\text{eff}})\, t_{(1+p)/2}(n) + (\nu_{\text{eff}} - n)\, t_{(1+p)/2}(n + 1) \tag{19.55}$$

The expanded uncertainty $U_p = k_p u_c(y)$ is estimated to have a coverage probability approximately equal to p.

EXAMPLE 19.31

Problem: Refer to the efficiency-calibration problem presented in Example 19.20 in Section 19.5.6. The efficiency for a radiation counter, ε, is calculated using the equation

$$\varepsilon = \frac{\overline{R}}{a_S}$$

where $\overline{R}$ (62.1854 $s^{-1} \cdot g^{-1}$) and its uncertainty (0.2301 $s^{-1} \cdot g^{-1}$) are determined from 15 replicate measurements (14 degrees of freedom), and a_S (150.0 Bq/g) and its uncertainty (2.0 Bq/g) are obtained from a calibration certificate. The calculated efficiency is 0.4146 and its combined standard uncertainty is 0.005736.

[21] The *GUM* uses the notation $t_p(\nu)$ to denote the $(1 + p) / 2$-quantile of a t-distribution with ν degrees of freedom (ISO, 1995), but the same notation in most statistical literature denotes the p-quantile (e.g., ISO, 1993). MARLAP follows the latter convention.

Assume the certificate states that the number of effective degrees of freedom for $u(a_S)$ is 12.5. Find the effective degrees of freedom for $u_c(\varepsilon)$, the coverage factor, $k_{0.95}$, that gives 95 % coverage probability, and the expanded uncertainty, $U_{0.95}$.

Solution: The component of the combined standard uncertainty of ε generated by $u(\overline{R})$ is

$$u_{\overline{R}}(\varepsilon) = \left|\frac{\partial \varepsilon}{\partial \overline{R}}\right| u(\overline{R}) = \frac{1}{a_S}\, u(\overline{R}) = \frac{0.2301\ \mathrm{s^{-1}\cdot g^{-1}}}{150.0\ \mathrm{Bq/g}} = 0.001534.$$

The component generated by $u(a_S)$ is

$$u_{a_S}(\varepsilon) = \left|\frac{\partial \varepsilon}{\partial a_S}\right| u(a_S) = \frac{|\overline{R}|}{a_S^2}\, u(a_S) = \frac{62.1854\ \mathrm{s^{-1}\cdot g^{-1}}}{(150.0\ \mathrm{Bq/g})^2}\,(2.0\ \mathrm{Bq/g}) = 0.0055276.$$

So, the number of effective degrees of freedom, v_{eff}, for $u_c(\varepsilon)$ is given by

$$v_{\mathrm{eff}} = \frac{u_c^4(\varepsilon)}{\dfrac{u_{\overline{R}}^4(\varepsilon)}{v_{\overline{R}}} + \dfrac{u_{a_S}^4(\varepsilon)}{v_{a_S}}} = \frac{(0.005736)^4}{\dfrac{0.001534^4}{15-1} + \dfrac{0.0055276^4}{12.5}} \approx 14.42.$$

Since 14.42 is not an integer, an interpolated *t*-factor may be used (see Table G.2 in Appendix G). The coverage factor for 95 % coverage probability is

$$k_{0.95} = (15 - 14.42)\,t_{0.975}(14) + (14.42 - 14)\,t_{0.95}(15) = (0.58)(2.145) + (0.42)(2.131) = 2.139.$$

So, the expanded uncertainty is

$$U_{0.95} = k_{0.95}\,u_c(\varepsilon) = (2.139)(0.005736) \approx 0.012.$$

19D.3 Poisson Counting Uncertainty

As stated in Section 19.5.2.2, the standard uncertainty in the number of counts, N, observed during a radiation measurement may often be estimated by $u(N) = \sqrt{N}$, according to the Poisson counting model. This method of evaluating the standard uncertainty is a Type B method; so, the effective degrees of freedom v for the evaluation should be determined from $\Delta u(N)$. The standard

deviation of $\sqrt{N}$ is always less than 0.65.[22] If N is greater than about 10, the standard deviation of $\sqrt{N}$ is approximately equal to 0.5, and, in this case, Equation 19.53 gives the estimate $v \approx 2N$. For smaller values of N, the same approximation is inadequate.

MARLAP recommends that the standard uncertainty, $u(N)$, and degrees of freedom, v, for a Poisson measured value, N, be estimated by

$$u(N) = \sqrt{N} \qquad \text{and} \qquad v = 2N \tag{19.56}$$

or, if very low counts are possible, by

$$u(N) = \sqrt{N + 1} \qquad \text{and} \qquad v = 2(N + 1) \tag{19.57}$$

If the expected count is greater than about 10, these formulas tend to give a coverage probability near the desired probability, p. When the expected count is small, the coverage probability tends to be greater than p.

Although the estimate $u(N) = \sqrt{N + 1}$ may be derived by the Bayesian approach to counting statistics assuming a flat prior distribution for the mean count (Friedlander et al., 1981), the recommended expressions for $u(N)$ and v in Equation 19.57 have been chosen for the purely practical reason that they are simple and seem to give satisfactory results. When the count is low, the assumptions underlying the Welch-Satterthwaite formula are usually violated, because the combined standard uncertainty is dominated by counting uncertainty, and the distribution of the count is not normal. However, even in this case, if the formula is used, the recommended expressions for $u(N)$ and v tend to give conservative results.

EXAMPLE 19.32

Problem: An alpha spectrometer is used to make a 60,000-second blank measurement followed by a 60,000-second sample measurement. The observed blank count is 2 and the observed sample count is 0. The net count rate is modeled as

[22] Taking the square root of a Poisson random variable is a common *variance-stabilizing transformation*, as described in Chapter 20 of *Experimental Statistics* (NBS, 1963). The stated (slightly conservative) upper bound for the standard deviation of $\sqrt{N}$ is based on calculations performed at the EPA's National Air and Radiation Environmental Laboratory, although the same approximate value may be determined by inspecting Figure 20-2 of NBS (1963). The precise calculation maximizes a function $f(x)$ whose value is the variance of the square root of a Poisson random variable with mean x. The first derivative of f is positive, decreasing and convex between $x = 0$ and the location of the maximum of the function at $x = 1.31895$; so, Newton's Method converges to the solution from below. The maximum value of f is found to be $(0.642256)^2$.

$$R_N = \frac{N_S}{t_S} - \frac{N_B}{t_B}$$

where

R_N is the net count rate (-3.333×10^{-5} s^{-1});
N_S is the sample count (0);
t_S is the sample count time (60,000 s);
N_B is the blank count (2); and
t_B is the blank count time (60,000 s).

Assume the only source of uncertainty is Poisson counting statistics. Determine the effective degrees of freedom for $u_c(R_N)$ and the coverage factor, $k_{0.95}$, that gives 95 % coverage probability.

Solution: Since very low counts are possible,

$$u(N_S) = \sqrt{N_S + 1} = 1 \qquad \text{and} \qquad v_{N_S} = 2(N_S + 1) = 2$$
$$u(N_B) = \sqrt{N_B + 1} = 1.732 \qquad \text{and} \qquad v_{N_B} = 2(N_B + 1) = 6$$

Then

$$u_c(R_N) = \sqrt{\frac{u^2(N_S)}{t_S^2} + \frac{u^2(N_B)}{t_B^2}} = \sqrt{\frac{1}{(60{,}000\text{ s})^2} + \frac{3}{(60{,}000\text{ s})^2}} = 3.333 \times 10^{-5}\text{ s}^{-1}$$

$$u_{N_S}(R_N) = \left|\frac{\partial R_N}{\partial N_S}\right| u(N_S) = \frac{1}{t_S}\sqrt{N_S + 1} = \frac{1}{60{,}000\text{ s}} = 1.667 \times 10^{-5}\text{ s}^{-1}$$

$$u_{N_B}(R_N) = \left|\frac{\partial R_N}{\partial N_B}\right| u(N_B) = \frac{1}{t_B}\sqrt{N_B + 1} = \frac{1.732}{60{,}000\text{ s}} = 2.887 \times 10^{-5}\text{ s}^{-1}$$

So, the number of effective degrees of freedom is

$$v_{eff} = \frac{u_c^4(R_N)}{\dfrac{u_{N_S}^4(R_N)}{v_{N_S}} + \dfrac{u_{N_B}^4(R_N)}{v_{N_B}}} = \frac{(3.333 \times 10^{-5})^4}{\dfrac{(1.667 \times 10^{-5})^4}{2} + \dfrac{(2.887 \times 10^{-5})^4}{6}} = 8$$

Then the coverage factor for a 95 % coverage probability is obtained from Table G.2 in Appendix G.

$$k_{0.95} = t_{0.975}(8) = 2.306$$

Notice that in this example, $\nu_{\text{eff}} = \nu_{N_S} + \nu_{N_B}$, but this equality would not hold if the count times for the sample and blank were unequal.

Also notice that the net count rate in this example is negative. Negative results may be common when environmental samples are analyzed for anthropogenic radionuclides.

19D.4 References

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ATTACHMENT 19E
Uncertainties of Mass and Volume Measurements

19E.1 Purpose

This attachment describes methods that may be used to evaluate the measurement uncertainty of a mass or liquid volume measurement. The first purpose of the attachment is to provide methods for more complete evaluations of these uncertainties than those presented earlier in Sections 19.5.9 and 19.5.10. A second purpose is to provide additional examples of uncertainty evaluations, and especially Type A evaluations based on historical data, as described in Section 19.4.2.1.

A third purpose of the attachment is to provide information about the sources of error in mass and volume measurements that may be useful for establishing reasonable quality control criteria. Even if one assumes that weighing and pipetting errors are negligible, the quality control for balances and volumetric apparatus should be strict enough to ensure the assumption is true. Some of the sources of error described below will undoubtedly be considered negligible in many radiochemical measurement processes, yet they may be too large to be ignored in a strict quality control program.

The existence of the attachment is not meant to imply that the uncertainties of mass and volume measurements tend to be relatively important in a radiochemistry laboratory. In fact the relative standard uncertainties of mass and volume measurements tend to be small if the measurements are made properly using appropriate instruments, and they may even be negligible in many cases when compared to other uncertainties associated with radiochemical analysis (e.g., see Section 19.5.12, “Subsampling”). However, one needs to know the performance limits of any measuring instrument. For example the measurement uncertainty may actually be relatively large if a laboratory balance is used to weigh a mass that is too small for it. The uncertainty may also be large in some cases if the sensitivity of the balance varies slightly between tare and gross measurements.

19E.2 Mass Measurements

19E.2.1 Considerations

Regardless of the methods used to evaluate balance measurement uncertainty, the results may be misleading unless the balance is well maintained and protected from external influences, such as drafts and sudden changes in pressure, temperature and humidity.

The appropriate method for evaluating the standard uncertainty of a mass measured using a balance depends on the type of balance, including its principles of calibration and operation, but the uncertainty of the measured result generally has components associated with balance sensitivity,

linearity, repeatability, and air buoyancy. Typically, the component associated with sensitivity includes the uncertainty of calibration and may include variability caused by changing environmental conditions, such as temperature. Other sources of uncertainty may include leveling errors and off-center errors, which should be controlled. Static electrical charges may also have an effect. Changes in mass (e.g., by absorption or evaporation of water) may be very significant for some materials.

19E.2.2 Repeatability

The repeatability of a balance is expressed as a standard deviation and is usually assumed to be independent of the load. It represents the variability of the result of zeroing the balance, loading a mass on the pan, and reading the indication.

Balance manufacturers provide specifications for repeatability, but a test of repeatability should also be part of the routine quality control for the balance (see ASTM E898). The simplest procedure for evaluating repeatability is to make a series of replicate measurements of a mass standard under "repeatability conditions." Repeatability conditions require one balance, one observer, one measurement location, and repetition during a short time period. For each measurement one must zero the balance, load the mass standard, and read the balance indication.

EXAMPLE 19.32 Suppose a laboratory balance has readability 0.0001 g, and, according to the manufacturer, the repeatability is also 0.0001 g. An analyst performs a series of 28 measurements using a 1-gram mass standard to check the repeatability. The results are listed below.

1.0001	0.9996	0.9999	1.0002
1.0002	0.9999	0.9999	1.0001
0.9998	0.9999	1.0000	1.0001
0.9999	0.9999	0.9999	1.0001
0.9998	0.9998	1.0000	0.9998
0.9996	0.9999	0.9999	1.0000
1.0002	0.9999	1.0001	1.0004

The analyst calculates the average, $\overline{W}$, and standard deviation, s, of these values (W_i) as follows.

$$\overline{W} = \frac{1}{28}\sum_{i=1}^{28} W_i = 0.9999607 \text{ g}$$

$$s = \sqrt{\frac{1}{28-1}\sum_{i=1}^{28} (W_i - \overline{W})^2} = 0.00018 \text{ g}$$

So, the analyst evaluates the repeatability to be 0.00018 g.

In this example, since the mass standard is so small, it may not be important that all the measurements be made during a short time period. Environmental factors produce relatively small day-to-day variability in the balance indication, and this variability may not be observable for a 1-gram load. So, the repeatability might be evaluated using the results of 28 routine quality control measurements.

A nested experimental design can also be used to evaluate both the repeatability and the day-to-day (or hour-to-hour) variability due to environmental factors. In this procedure, one makes a series of replicate measurements with the same mass standard each day for a number of days, or perhaps in a morning session and afternoon session each day. Ideally, one should use a mass near the capacity of the balance to obtain the most reliable estimate of day-to-day variability, but almost any mass in the balance's range will do for an estimate of repeatability. The repeatability standard deviation is estimated by

$$s_r = \sqrt{\frac{1}{K(J-1)} \sum_{k=1}^{K} \sum_{j=1}^{J} (x_{k,j} - \bar{x}_k)^2} \tag{19.58}$$

where

s_r is the estimated repeatability standard deviation;
J is the number of repetitions per session;
K is the number of sessions;
$x_{k,j}$ is the j^{th} result obtained in the k^{th} session; and
$\bar{x}_k$ is the average of all the results in the k^{th} session.

The repeatability standard deviation determined by this method is a Type A standard uncertainty with $K(J - 1)$ degrees of freedom.

19E.2.3 Environmental Factors

The correct method for evaluating the balance measurement uncertainty due to environmental factors depends strongly on the method and frequency of calibration. Some balances, especially newer models, have internal calibration masses, which allow frequent calibration with only the push of a button. Other balances use external calibration mass standards and require more care in the calibration process. Balances of the latter type in many cases are calibrated infrequently. If a balance is calibrated immediately before a measurement, then the uncertainty due to environmental factors can be considered to be zero. However, if hours or days pass between the time of calibration and the time of measurement, then this uncertainty component may be significant. For the remainder of this subsection, the latter case is assumed.

Given the nested experimental data from the preceding section, one may estimate the variability due to environmental factors (day-to-day or hour-to-hour variability) as follows.[23]

$$s_{\text{env}}^2 = \frac{1}{K-1}\sum_{k=1}^{K}(\bar{x}_k - \bar{\bar{x}})^2 - \frac{s_r^2}{J} \tag{19.59}$$

where

s_{env}^2 is the estimated variance due to environmental factors and

$\bar{\bar{x}}$ is the grand average of all the data (the average of the $\bar{x}_k$).

If s_{env}^2 is found to be positive, then s_{env} is estimated by its square root; otherwise, s_{env} is assumed to be zero. One estimates the relative component of standard uncertainty of a measured mass due to environmental factors by

$$\varphi_{\text{env}} = \frac{s_{\text{env}}}{m_{\text{check}}} \tag{19.60}$$

where m_{check} is the mass of the standard used in the experiment.

If the variability due to environmental factors is large, its magnitude can also be estimated by weighing a heavy mass standard once per day for a number of days, or perhaps once in the morning and once in the afternoon of each day. Clearly, the observed variability will include the effects of both environmental factors and repeatability, but environmental factors presumably dominate when a heavy mass is weighed, because their effect is proportional to the mass, whereas the repeatability is essentially constant at all masses. So, the observed variability can be used as a reasonable estimate of the variability due to environmental factors alone.

EXAMPLE 19.33 Suppose a laboratory balance has readability 0.0001 g, repeatability 0.0001 g, and a capacity of approximately 110 g. An analyst performs QC measurements using masses of 1, 50, and 100 g. The results obtained using the 100-gram mass standard during a certain time period are as follows:

99.9992	99.9989	99.9986	100.0008
100.0001	99.9990	100.0002	100.0010
99.9993	99.9988	100.0003	99.9975
99.9989	100.0015	99.9989	99.9981
99.9992	99.9992	100.0012	100.0009
100.0002	99.9997	100.0002	100.0005
99.9989	99.9990	100.0011	99.9991

[23] An F-test may be used to test for the presence of variance due to environmental factors. If this variance is zero, then the quantity $Js_{\bar{x}}^2 / s_r^2$, where $s_{\bar{x}}^2$ denotes the experimental variance of the averages $\bar{x}_i$, may be assumed to have an F-distribution with $K - 1$ numerator degrees of freedom and $K(J - 1)$ denominator degrees of freedom.

The average, $\overline{W}$, and standard deviation, $s(W_i)$, of these values are calculated below.

$$\overline{W} = \frac{1}{28}\sum_{i=1}^{28} W_i = 99.9996536 \text{ g}$$

$$s(W_i) = \sqrt{\frac{1}{28-1}\sum_{i=1}^{28}(W_i - \overline{W})^2} = 0.001016 \text{ g}$$

Since this standard deviation is much larger than the repeatability, 0.0001 g, essentially all of the variability may be attributed to environmental factors. The estimate is slightly inflated by the balance's repeatability variance, but the difference in this case is only about 0.5 % of the value shown. So, the relative standard uncertainty due to environmental factors is estimated as

$$\varphi_{\text{env}} = \frac{0.001016}{100} \approx 1.0 \times 10^{-5}$$

19E.2.4 Calibration

The uncertainty of calibration includes components associated with the mass standard or standards, repeatability, and variability due to environmental factors.

When a precision mass standard is used for calibration, the standard uncertainty of its mass is generally negligible. However, the uncertainty may be evaluated if necessary from the specified mass tolerance. For example, a 100-gram ASTM Class-1 mass standard has a tolerance of 0.00025 g, which may be assumed to represent the half-width of a triangular distribution centered at zero (ASTM E617). The standard uncertainty may be found by dividing this tolerance by $\sqrt{6}$ and is approximately 0.00010 g, or 1.0×10^{-6} when expressed in relative terms.

The total relative standard uncertainty of a mass measurement due to calibration may be estimated as follows.

$$\varphi_{\text{cal}} = \sqrt{\varphi_{\text{env}}^2 + \frac{s_{\text{r}}^2 + \delta_{\text{cal}}^2/6}{m_{\text{cal}}^2}} \tag{19.61}$$

where

φ_{cal} is the total relative standard uncertainty of a balance measurement due to calibration;
φ_{env} is the relative standard uncertainty due to environmental factors;
s_{r} is the repeatability standard deviation;
δ_{cal} is the tolerance for the mass of the calibration standard; and
m_{cal} is the mass of the standard used for calibration.

If environmental conditions are not well-controlled, φ_{env} may tend to dominate the other components here, since both s_r and δ_{cal} are much smaller than m_{cal}.

19E.2.5 Linearity

The linearity of a balance should be specified by the manufacturer as a tolerance, a_L, which represents the maximum deviation of the balance indication from the value that would be obtained by linear interpolation between the calibration points. Routine quality control should ensure that the linearity remains within acceptable limits.

The *Eurachem/CITAC Guide: Quantifying Uncertainty in Analytical Measurement* recommends that the linearity tolerance a_L be treated as the half-width of a rectangular distribution and that a_L therefore be divided by $\sqrt{3}$ to obtain the standard uncertainty (Eurachem, 2000). However, since the linearity error is likely to vary as a sinusoidal function of the load, as illustrated in Figure 19.13, the divisor $\sqrt{2}$ may be more appropriate. So, the standard uncertainty due to linearity for a simple mass measurement may be evaluated as $a_L / \sqrt{2}$. Whether one uses $\sqrt{3}$ or the more conservative value $\sqrt{2}$ depends partly on how conservative one believes the estimate of a_L to be.

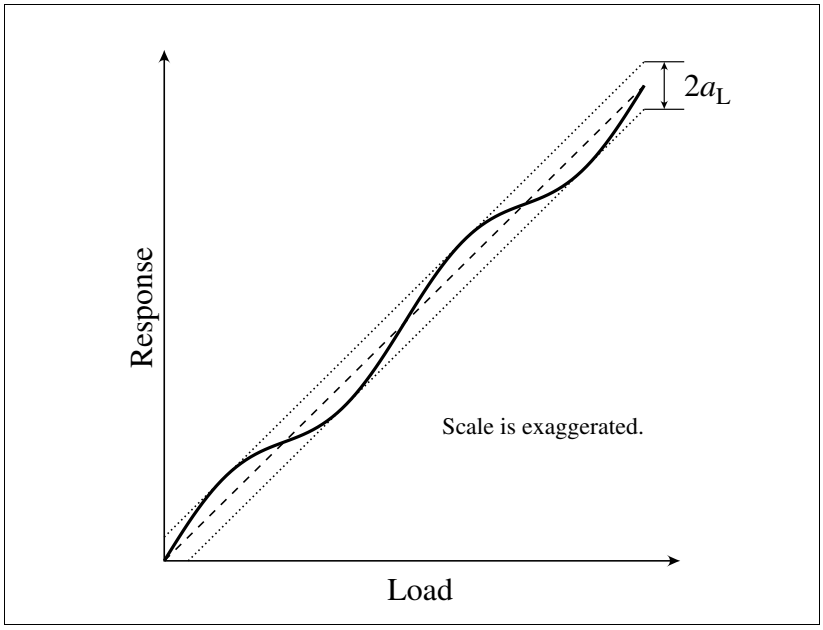

FIGURE 19.13 — Nonlinear balance response curve

19E.2.6 Gain or Loss of Mass

When gain or loss of mass is a relevant issue, as for example when the material being weighed is a volatile liquid or a hygroscopic solid, the mass should be treated as a function of time. One method of determining this function is to weigh the material at different times, recording both the

time and the observed mass, and fit a line or curve to the resulting data points. One can then calculate the mass at a particular time of interest (e.g., before any gain or loss occurred, or perhaps during the period when the material was in a radiation counter). If possible, it is better to weigh the material both before and after the time of interest to avoid extrapolating the curve to points in time where its accuracy may be unknown. However, in some situations extrapolation may be necessary, as for example when determining the dry mass of a hygroscopic precipitate.

The standard uncertainty of a mass calculated in this manner includes components for curve-fitting errors.

19E.2.7 Air-Buoyancy Corrections

Air-buoyancy corrections are not often performed in radiochemistry laboratories, because they are usually negligible in comparison to the overall uncertainty of the result. However, when the measurand is the mass itself and not some other quantity such as a radionuclide concentration whose calculated value depends on the mass, buoyancy corrections may be important. Failure to correct for air buoyancy when weighing water, for example, introduces a relative error of approximately −0.1 %, which may be much larger than the standard uncertainty of the uncorrected mass (e.g., when weighing a gram or more of an aqueous solution on a typical four-place analytical balance).

When a buoyancy-correction factor is used, the true mass is estimated as follows.

$$m = I_{\text{net}}\, B \tag{19.62}$$

where

$$B = \frac{1 - \varrho_{\text{A,C}} / \varrho_{\text{C}}}{1 - \varrho_{\text{A,M}} / \varrho_{\text{M}}} \tag{19.63}$$

and

m is the corrected value for the mass of the material being weighed;
I_{net} is the net balance indication;
B is the buoyancy-correction factor;
ϱ_{M} is the density of the material being weighed;
ϱ_{AM} is the density of the air at the time the material is weighed;
ϱ_{C} is the density of the calibration mass standard; and
ϱ_{AC} is the density of the air at the time of calibration.

The standard uncertainty of B may be obtained as follows.

$$\frac{u^2(B)}{B^2} = \frac{\dfrac{u^2(\varrho_{AC})}{\varrho_{AC}^2} - 2\dfrac{u(\varrho_{AC},\varrho_C)}{\varrho_{AC}\varrho_C} + \dfrac{u^2(\varrho_C)}{\varrho_C^2}}{\left(\dfrac{\varrho_C}{\varrho_{AC}} - 1\right)^2} + \frac{\dfrac{u^2(\varrho_{AM})}{\varrho_{AM}^2} - 2\dfrac{u(\varrho_{AM},\varrho_M)}{\varrho_{AM}\varrho_M} + \dfrac{u^2(\varrho_M)}{\varrho_M^2}}{\left(\dfrac{\varrho_M}{\varrho_{AM}} - 1\right)^2} \tag{19.64}$$

Evaluation of this uncertainty requires estimates of ϱ_M, ϱ_C, ϱ_{AM} and ϱ_{AC} as well as their standard uncertainties and covariances. The covariance $u(\varrho_{AC}, \varrho_C)$ is usually zero or negligible, and $u(\varrho_{AM}, \varrho_M)$ also is usually negligible if the material being weighed is a solid.

Clearly, $u(B)$ tends to be no more significant in a radiochemical measurement than the factor B itself is, but it may generate a large fraction of the uncertainty of the mass, m, since the uncertainty of the mass is often tiny.

The density of air (ϱ_A) depends on temperature, pressure, and humidity, as shown in the following equation.

$$\varrho_A = \varrho_0 \left(\frac{273.15\ \text{K}}{273.15\ \text{K} + t}\right)\left(\frac{p - (0.3783)\varphi e_S}{101.325\ \text{kPa}}\right) \tag{19.65}$$

where

ϱ_A is the density of air;
ϱ_0 is the density of dry air at 0 °C and 101.325 kPa (1 atm);
t is the Celsius temperature;
p is the barometric pressure;
φ is the relative humidity (a fraction between 0 and 1); and
e_S is the saturation vapor pressure of water at temperature t.

The vapor pressure, e_S, is a nonlinear function of t, but it can be approximated by a linear function in the range of temperatures typically encountered in the laboratory. When this approximation is made, the resulting equation for the air density may be written as follows.

$$\varrho_A = \frac{ap - \varphi(bt - c)}{273.15\ \text{K} + t} \tag{19.66}$$

where

a = 3.48589×10^{-3} K · s^2 / m^2;
b = 2.5211151×10^{-4} g / mL; and
c = 2.0590571×10^{-3} K · g / mL.