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Standard Guide for Evaluating and Expressing the Uncertainty of Radiochemical Measurements[1]

This standard is issued under the fixed designation D8293; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide provides concepts, terminology, symbols, and recommendations for the evaluation and expression of the uncertainty of radiochemical measurements of water and other environmental media by testing laboratories. It applies to measurements of radionuclide activities, including gross activities, regardless of whether they involve chemical preparation of the samples.

1.2 This guide does not provide a complete tutorial on measurement uncertainty. Interested readers should refer to the documents listed in Section 2 and References for more information. See, for example, GUM, QUAM, Taylor and Kuyatt (**1**)[2], and Chapter 19 of MARLAP (**2**).

1.3 The system of units for this guide is not specified. Dimensional quantities in the guide are presented only as illustrations of calculation methods. The examples are not binding on products or test methods treated.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1129 Terminology Relating to Water

D7902 Terminology for Radiochemical Analyses

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

E288 Specification for Laboratory Glass Volumetric Flasks

E438 Specification for Glasses in Laboratory Apparatus

E456 Terminology Relating to Quality and Statistics

E542 Practice for Gravimetric Calibration of Laboratory Volumetric Instruments

E617 Specification for Laboratory Weights and Precision Mass Standards

E898 Practice for Calibration of Non-Automatic Weighing Instruments

E969 Specification for Glass Volumetric (Transfer) Pipets

E1272 Specification for Laboratory Glass Graduated Cylinders

E2655 Guide for Reporting Uncertainty of Test Results and Use of the Term Measurement Uncertainty in ASTM Test Methods

2.2 *ANSI Standards:*[4]

ANSI N42.23 Measurement and Associated Instrumentation Quality Assurance for Radioassay Laboratories

2.3 *BIPM Documents:*

GUM: JCGM 100:2008 Evaluation of measurement data—Guide to the expression of uncertainty in measurement[5]

JCGM 101:2008 Evaluation of measurement data—

[1] This guide is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

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[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[5] Available from www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf, accessed January 2021.

Supplement 1 to the "Guide to the expression of uncertainty in measurement"—Propagation of distributions using a Monte Carlo method[6]

JCGM 102:2011 Evaluation of measurement data—Supplement 2 to the "Guide to the expression of uncertainty in measurement"—Extension to any number of quantities[7]

JCGM 200:2008 International vocabulary of metrology—Basic and general concepts and associated terms (VIM)[8]

2.4 *OIML Documents:*

OIML D 28: 2004 (E) Conventional value of the result of weighing in air[9]

2.5 *Eurachem Guides:*

QUAM Quantifying Uncertainty in Analytical Measurement, Eurachem/CITAC Guide CG 4, Third edition[10]

3. Terminology

3.1 *Definitions:*

3.1.1 *conventional mass, n*—property of a body equal to the mass of a standard of density 8000 kg/m^3 that exactly balances that body when weighed in air of density 1.2 kg/m^3 at 20 °C, as defined in Specification E617 and International Document OIML D 28.

3.1.2 *index of dispersion, J, n*—ratio of the variance of a random variable or probability distribution to its mean; also called simply the *variance-to-mean ratio*.

3.1.3 *normalized absolute difference, NAD, n*—absolute value of the *normalized difference*.

3.1.4 *normalized difference, n*—quotient of the difference between two measured values and the combined standard uncertainty of that difference.

3.1.4.1 *Discussion*—The *normalized difference* is similar to a *zeta score* (ζ *score*) as that term is commonly used in proficiency testing. Other terms may be used for the same concept.

3.1.5 *relative sensitivity factor, n*—ratio of the relative change in an output quantity to a small relative change in a specified input quantity.

3.1.6 For definitions of many other terms used in this guide, refer to Terminology D1129, Terminology D7902, Practice E177, Terminology E456, Guide E2655, Test Method E898, JCGM 200, and the GUM.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *minimum detectable value, n*—smallest true value of a nonnegative statistical parameter that ensures a specified high probability of a positive result in a specified hypothesis test for that parameter.

3.2.2 *subsampling factor, F_S, n*—ratio of the massic or volumic activity of a subsample to that of the sample from which it is taken.

4. Summary of Practice

4.1 General rules and recommendations for evaluating and expressing measurement uncertainty are given, followed by more detailed discussions of uncertainty evaluation, propagation, and reporting. Topics include Type A and Type B evaluations of uncertainty, correlations, coverage factors, rounding rules, and shorthand formats for expressing uncertainty. Guidelines for determining the practical significance of uncertainty components are presented. Next, some of the most commonly encountered components of uncertainty in radiochemical measurements are discussed, with suggested methods of evaluation and examples. Topics include counting uncertainty, background, chemical yield, counting efficiency (calibration), aliquot sizes, decay and ingrowth factors, and subsampling. A few other miscellaneous topics, such as the calculation of weighted averages with uncertainties and non-Poisson counting, are also included. Special topics such as uncertainty budgets and evaluation of uncertainties for mass measurements are presented in the appendices, followed by several applications and worked-out examples.

5. Significance and Use

5.1 This guide is intended to help testing laboratories and the developers of methods and software for those laboratories to apply the concepts of measurement uncertainty to radiochemical analyses.

5.2 The result of a laboratory measurement never exactly equals the true value of the measurand. The difference between the two is called the *error* of the measurement. An estimate of the possible magnitude of this error is called the *uncertainty* of the measurement. While the error is primarily a theoretical concept, since its value is never known, the uncertainty has practical uses. Together, the measured value and its uncertainty allow one to place bounds on the likely true value of the measurand.

5.3 Reliable measurement-based decision making requires not only measured values but also an indication of their uncertainty. Traditionally, significant figures have been used with varying degrees of success to indicate implicitly the order of magnitude of measurement uncertainties; however, reporting an explicit uncertainty estimate with each result is more reliable and informative, and is considered an industry-standard best practice.

6. Procedure

6.1 *General Rules and Recommendations:*

6.1.1 Whenever a laboratory reports the result of a radioanalytical measurement, the report should include an explicit estimate of the measurement uncertainty. The measured value and its uncertainty together constitute the overall result of the measurement. General guidance for evaluating and expressing measurement uncertainty is provided in the GUM and in Guide E2655. Supplemental guidance is given in JCGM 101 and JCGM 102. More specific guidance for radiochemical

[6] Available from www.bipm.org/utils/common/documents/jcgm/JCGM_101_2008_E.pdf, accessed January 2021.

[7] Available from www.bipm.org/utils/common/documents/jcgm/JCGM_102_2011_E.pdf, accessed January 2021.

[8] Available from www.bipm.org/utils/common/documents/jcgm/JCGM_200_2012.pdf, accessed January 2021.

[9] Available from www.oiml.org/en/files/pdf_d/d028-e04.pdf, accessed January 2021.

[10] Available from eurachem.org/index.php/publications/guides/quam, accessed January 2021.

measurements, including a list of recommended practices for radiation laboratories, can be found in MARLAP (**2**). Guidance for chemical measurement laboratories, much of which is also applicable to radiochemistry, is provided in QUAM. Ref (**3**) also provides a set of detailed examples related to radiochemical analyses.

6.1.2 Laboratories performing radiochemical analyses should follow the guidance of the GUM and its supplements, which provide standards for terminology, notation, and methodology. The use of standard terminology and notation promotes clear communication between laboratories and their clients. Furthermore, the use of common methodologies promotes comparability of results and effective decision-making based on those results.

6.1.3 Generally, the reported uncertainty represents an estimate of the "total uncertainty" of the measurement, which accounts for all significant sources of inaccuracy in the result. However, for legal or contractual reasons, a laboratory may sometimes be required to report only a partial uncertainty estimate. For example, U.S. laboratories analyzing drinking water for compliance with the U.S. EPA's National Primary Drinking Water Regulations may be required to report the *counting uncertainty* for each result (see 6.12).

6.1.4 The estimate of total uncertainty accounts for both random and systematic effects in the measurement process, but not spurious errors such as those due to instrument malfunctions and human blunders, which represent a loss of statistical control of the process. Statistical control of the measurement process is a prerequisite for meaningful uncertainty evaluations.

6.1.5 The uncertainty of a measured value should always be positive, never zero or negative.

6.1.6 Typically, the result of a radiochemical analysis is not measured directly but is instead calculated from other measured quantities, called *input quantities*, using a *mathematical model* of the measurement process. In this context, the final calculated result is called the *output quantity*. The uncertainty of each input is first estimated in the form of a standard deviation, called the *standard uncertainty*. The laboratory then obtains the standard uncertainty of the final result by combining the standard uncertainties of the inputs according to general mathematical rules applied to the measurement model. Mathematically combining uncertainties in this manner is called *propagation of uncertainty*. A standard uncertainty obtained by uncertainty propagation is also called a *combined standard uncertainty*.

6.1.7 The laboratory may report the uncertainty of the result either as the combined standard uncertainty or a specified multiple thereof, called an *expanded uncertainty*. The analysis report should always specify which type of uncertainty is being reported, and if it is an expanded uncertainty, the report should specify the multiplicative factor, called the *coverage factor* and denoted by k. For an expanded uncertainty, the report should also state the approximate *coverage probability*, defined as the probability p that the interval about the measured value described by its expanded uncertainty will contain the true value of the measurand.

6.2 *Overview of Procedure:*

6.2.1 Let the measurement model be given abstractly by the equation:

$$Y = f(X_1, X_2, \ldots, X_N) \tag{1}$$

where Y denotes the output quantity, which is also the measurand, $X_1, X_2, \ldots, X_N$ denote the input quantities, and f is the *measurement function*. In practice the measurement model may be implemented as one or more equations—for example, in a spreadsheet or specialized software application. What matters is that there are unambiguous rules for calculating the output quantity from the input quantities. For a less abstract example of a measurement model, see Eq 38 in 6.11.

NOTE 1—The distinction between input quantities and output quantities depends on context. An input quantity in one measurement may be an output quantity from another measurement.

6.2.2 When the laboratory makes a measurement, it finds particular values $x_1, x_2, \ldots, x_N$ for the input quantities. These values may be called *input estimates*. The lab applies the measurement function to the input estimates to calculate the *output estimate*.

$$y = f(x_1, x_2, \ldots, x_N) \tag{2}$$

This output estimate y is the measured value.

NOTE 2—In Eq 1, upper-case symbols (Y or X_i) denote random variables or abstract quantities, while in Eq 2, lower-case symbols (y or x_i) denote particular values of those random variables or quantities. This distinction is maintained when describing techniques for uncertainty evaluation and propagation; however, in most applications of these equations, the distinction is dropped, and the same symbols are used for both the random variables and their values.

6.2.3 When the laboratory determines each input estimate x_i, it determines the associated standard uncertainty $u(x_i)$, as described in 6.3. If necessary, the lab also estimates the covariance of any pair of correlated input estimates, x_i and x_j. Given this information, the laboratory then mathematically combines the uncertainties and covariances using standard techniques for uncertainty propagation (6.4 – 6.6) to obtain the combined standard uncertainty $u_c(y)$.

6.2.4 The laboratory optionally multiplies $u_c(y)$ by a coverage factor k, described in 6.7, to obtain an expanded uncertainty U. It then rounds and reports the result y with either the combined standard uncertainty $u_c(y)$ or the expanded uncertainty U, as described in 6.8.

6.3 *Evaluating Measurement Uncertainties:*

6.3.1 The GUM classifies methods for direct evaluation of uncertainty as either *Type A* or *Type B*. A Type A evaluation is an evaluation of standard uncertainty by the statistical analysis of one or more series of observations. By definition, any evaluation of standard uncertainty that is not Type A is Type B.

6.3.2 An uncertainty evaluated by a Type A method may be called a *Type A uncertainty*, and an uncertainty evaluated by a Type B method may be called a *Type B uncertainty*. However, the rules of uncertainty propagation make no distinction between the two types: all uncertainties are propagated in the same manner.

6.3.3 Any Type A evaluation of uncertainty has a well-defined number of statistical degrees of freedom, as indicated in the examples that follow.

6.3.4 One of the simplest examples of a Type A evaluation of uncertainty is the estimation of the standard uncertainty of a measured value q by the *experimental standard deviation* of repeated observations made in the same manner. If the observed values are $q_1, q_2, \ldots, q_n$, the arithmetic mean (average) and the experimental standard deviation are given by:

$$\overline{q} = \frac{1}{n}\sum_{k=1}^{n} q_k \quad \text{and} \quad s(q_k) = \sqrt{\frac{1}{n-1}\sum_{k=1}^{n}(q_k - \overline{q})^2} \tag{3}$$

The standard uncertainty of any single observation, $u(q_k)$, equals $s(q_k)$. The number of degrees of freedom for this evaluation is $n - 1$.

Example—To evaluate the repeatability of an electronic balance (see 6.17.4), an analyst makes a series of 20 measurements of a 1-gram weight, obtaining the values $w_1, w_2, \ldots, w_{20}$ listed below (all values in grams).

1.0002	0.9997	0.9999	1.0001	0.9999
1.0000	1.0000	0.9996	0.9997	0.9999
1.0000	0.9999	0.9998	0.9997	1.0000
1.0000	1.0002	1.0000	1.0000	0.9999

The analyst then calculates the average and standard deviation of the values as follows:

$$\begin{aligned} \overline{w} &= \frac{1}{20}\sum_{k=1}^{20} w_k \\ &= \frac{19.9985\ \text{g}}{20} \\ &= 0.999925\ \text{g} \end{aligned} \tag{4}$$

$$\begin{aligned} s(w_k) &= \sqrt{\frac{1}{20-1}\sum_{k=1}^{20}(w_k - 0.999925\ \text{g})^2} \\ &= \sqrt{\frac{4.975 \times 10^{-7}\ \text{g}^2}{19}} \\ &= 0.00016\ \text{g} \end{aligned} \tag{5}$$

The standard deviation $s(w_k)$ is an estimate of the balance's repeatability. (See also X2.1.)

6.3.5 Another simple example of a Type A evaluation is the estimation of the uncertainty of an average measured value, $\bar{q}$, by the *experimental standard deviation of the mean*, $s(\bar{q})$, also known as the "standard error" of the mean. Given repeated observations $q_1, q_2, \ldots, q_n$, the experimental standard deviation of the mean is given by:

$$s(\overline{q}) = \frac{s(q_k)}{\sqrt{n}} = \sqrt{\frac{1}{n(n-1)}\sum_{k=1}^{n}(q_k - \overline{q})^2} \tag{6}$$

When the average value $\bar{q}$ is used to estimate a quantity, $u(\bar{q})$ equals $s(\bar{q})$. The number of degrees of freedom is $n - 1$.

6.3.6 A typical use for $s(\bar{q})$ is to evaluate the uncertainty of a particular measured quantity from repeated observations of that quantity. A typical use for $s(q_k)$ is to estimate the uncertainties of unrepeated future observations of particular quantities of the same type measured by the same process, as in the example of balance repeatability above.

6.3.7 One may use $s(\bar{q})$ to estimate the standard uncertainty of an average $\bar{q}$ even when the individual observations q_k have different variances, although in such cases the Type A degrees of freedom, $n - 1$, may overestimate the quality of the uncertainty evaluation. On the other hand, the use of $s(q_k)$ presumes that all the observations q_k as well as future observations from the same measurement process have the same variance.

6.3.8 A Type A evaluation of the covariance of two measured quantities involves a statistical analysis of a series of paired observations of those quantities. To evaluate the *experimental covariance* of a pair of observed values, use the equation:

$$s(q_k, r_k) = \frac{1}{n-1}\sum_{k=1}^{n}(q_k - \overline{q})(r_k - \overline{r}) \tag{7}$$

where q_k and r_k denote two simultaneously observed values and $\bar{q}$ and $\bar{r}$ denote the average values. To evaluate the experimental covariance of the means, divide the preceding estimate by n, as shown below:

$$s(\overline{q}, \overline{r}) = \frac{1}{n(n-1)}\sum_{k=1}^{n}(q_k - \overline{q})(r_k - \overline{r}) \tag{8}$$

6.3.9 Line- or curve-fitting by ordinary least squares (OLS) can also be used for a Type A evaluation of standard uncertainty. Since OLS is most properly applied to homoscedastic data, in which the variance for each data point is the same, good examples of its use in radiochemistry seem to be rare. However, X6.5 describes an example in which a logarithmic transformation is applied to data assumed to have approximately the same *relative* variance, resulting in transformed data with nearly constant variance. OLS is then used to fit a straight line to the transformed data and to estimate its Type A standard uncertainty.

6.3.10 A Type B evaluation of uncertainty typically involves an assumed probability distribution for the quantity being estimated. The distribution is determined by the estimated value q and in most cases by one or more other parameters, often including a tolerance that describes an interval about q within which the true value is believed to lie. The standard uncertainty $u(q)$ equals the standard deviation of the assumed distribution.

6.3.11 Type B evaluations are commonly used for the uncertainties of inputs for which repeated observations are impractical. Examples of such inputs include the values for certified reference materials, radioactive half-lives, and capacities of volumetric glassware. Since it is common for a testing lab to count a prepared sample test source only once, Type B (Poisson) evaluations of counting uncertainty are also common. In fact, Type B evaluations of uncertainty are probably far more common than Type A evaluations at most testing labs.

6.3.12 Appendix X1 describes Type B evaluations based on normal, rectangular, triangular, and U distributions. Evaluations based on Poisson distributions are described in 6.12.

6.3.13 The statistical analysis that implements a Type A evaluation of a standard uncertainty $u(x_i)$ always has an associated number of degrees of freedom, ν_i. The larger the number ν_i, the smaller the relative standard uncertainty of $u(x_i)$ as an estimator for the true standard deviation of the distribution of X_i. Based on the approximate mathematical relationship between Type A degrees of freedom and the relative standard

uncertainty of $u(x_i)$, the number of degrees of freedom for a Type B evaluation is defined to be:

$$\nu_i = \frac{1}{2}\left(\frac{\Delta u(x_i)}{u(x_i)}\right)^{-2} \quad (9)$$

where $\Delta u(x_i)$ denotes the standard uncertainty of $u(x_i)$, and $\Delta u(x_i)/u(x_i)$ is its relative standard uncertainty—the "uncertainty of the uncertainty." While this equation is only approximately true for Type A degrees of freedom, it serves as a definition for Type B degrees of freedom.

6.3.14 Table 1 gives examples of Type B degrees of freedom calculated using Eq 9. Note that the calculated number ν_i may not be an integer. It may also be infinite if $\Delta u(x_i)$ is considered to be zero, a case which is most likely when the Type B uncertainty is based on a rectangular distribution with a well-known tolerance, as described in Appendix X1—for example, the uncertainty due to rounding a number. For the degrees of freedom associated with Poisson uncertainty evaluations, see 6.12.11. For other Type B evaluations, the value of $\Delta u(x_i)$ is often based on available knowledge and professional judgment.

6.4 *Propagation of Uncertainty:*

6.4.1 After the uncertainties and covariances of the input estimates are determined, they are combined mathematically using uncertainty propagation to obtain the combined standard uncertainty of the output estimate.

6.4.2 A *component* of the combined standard uncertainty is a portion of the total uncertainty attributed to a particular cause, such as counting statistics, standards, tracers, volumetric glassware, and subsampling, to name only a few. The combined standard uncertainty can be interpreted as a combination of its components.

6.4.3 Components of the combined standard uncertainty do not add linearly in the manner of a simple sum; instead, they add "in quadrature." To add components in quadrature, one squares each component, adds the squares, and takes the square root of the resulting sum. This operation is described below in more detail.

6.4.4 The laboratory evaluates the standard uncertainty of each input estimate x_i. An uncertainty $u(x_i)$ may be evaluated directly by a Type A or Type B method, as described in 6.3 and Appendix X1. However, it often happens that an input estimate x_i is obtained as the output estimate from another measurement, in which case its uncertainty is typically obtained by uncertainty propagation. In fact, when the measurement function $f(X_1, X_2, \ldots, X_N)$ is complicated enough, it is common to break the full expression down into subexpressions, each of which in effect represents a simpler measurement function to which the rules of uncertainty propagation are applied first. For example, see 6.11, where four of the input estimates are calculated from other measured values.

6.4.5 The combined standard uncertainty of the output estimate y, denoted by $u_c(y)$, is found using the *law of propagation of uncertainty* (also called simply the *uncertainty propagation formula*).

$$u_c(y) = \sqrt{\sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + \cdots} \quad (10)$$

The partial derivatives $\partial f/\partial x_i$, called *sensitivity coefficients*, are the first partial derivatives of f, evaluated at or near the observed values of the x_i. Each sensitivity coefficient $\partial f/\partial x_i$ represents the ratio of the change in the value of the output y to a tiny change in the value of a single input x_i. In measurement reports, a sensitivity coefficient $\partial f/\partial x_i$ is commonly denoted by c_i.

NOTE 3—The partial derivative $\partial f/\partial x_i$ may also be denoted by $\partial y/\partial x_i$.

6.4.6 Ideally, the partial derivatives $\partial f/\partial x_i$ would be evaluated at the true values of the input quantities X_i, if they were known, but since they are unknown, the evaluation uses the observed values x_i. In some cases, especially when measurements are performed for purposes of quality control, there may be better prior estimates of the true values, which can be used to evaluate the sensitivity coefficients.

6.4.7 Fig. 1 illustrates a partial derivative of a function of two variables. The figure depicts the function as a curved surface, $y = f(x_1, x_2)$. A plane perpendicular to the x_1-axis slices the surface at a chosen value of x_1, intersecting the surface in a curve. The value of $\partial f/\partial x_2$ at any point on the curve equals the slope of the tangent line at that point.

6.4.8 The ellipsis (. . .) in Eq 10 indicates the possibility of additional terms under the radical. Additional terms appear when input estimates are correlated with each other (see 6.5).

6.4.9 The component of the combined standard uncertainty $u_c(y)$ generated by the uncertainty of an input estimate x_i can be found as follows:

$$u_i(y) = \left|\frac{\partial f}{\partial x_i}\right| u(x_i) = |c_i| u(x_i) \quad (11)$$

TABLE 1 Type B Degrees of Freedom

$\Delta u(x_i) / u(x_i)$	ν_i
50 %	2
33.3 %	4.5
25 %	8
20 %	12.5
10 %	50
5 %	200
0 %	∞

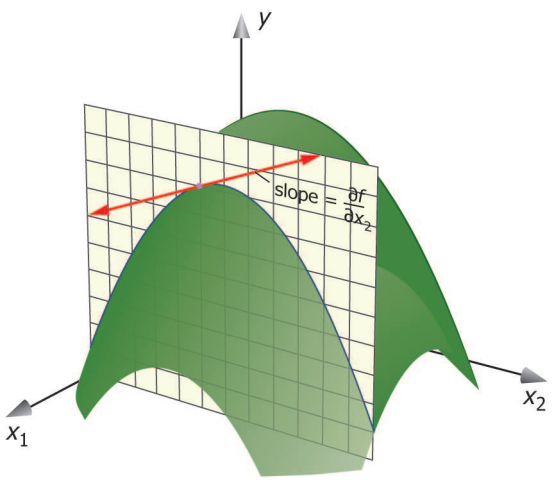

FIG. 1 Partial Derivative $\partial f / \partial x_2$ of a Function $y = f(x_1, x_2)$

Here $u_i(y)$ denotes the component of $u_c(y)$ generated by $u(x_i)$. The law of propagation of uncertainty can then be written explicitly in terms of uncertainty components, as shown below:

$$u_c(y) = \sqrt{\sum_{i=1}^{N} u_i^2(y) + \cdots} \quad (12)$$

6.4.10 After the combined standard uncertainty $u_c(y)$ is calculated, it may be multiplied by a *coverage factor*, k, to obtain an *expanded uncertainty*, $U = k \cdot u_c(y)$. The expanded uncertainty describes an interval $y \pm U$ that is believed to have a high probability of containing the true value of the measurand. The value of k should be greater than 1 and typically ranges from 2 to 3. If the distribution of the result is normal (Gaussian) and if the standard uncertainty is a good estimate of the true standard deviation, a coverage factor of 2 provides approximately 95 % coverage probability, and a coverage factor of 3 provides more than 99 % coverage probability. See 6.7 for more information about determining a coverage factor to provide a specified coverage probability p.

NOTE 4—A testing lab should choose the coverage factor $k = 2$ or the coverage probability $p = 95$ % by default unless there are compelling reasons to do otherwise.

6.4.11 Fig. 2 applies a geometric analogy to illustrate uncertainty propagation for a hypothetical measurement equation $y = f(x_1, x_2)$ with two input quantities. The width and height of the rectangle represent the two uncertainty components while the diagonal represents the combined standard uncertainty. In this analogy, Eq 12 for two uncorrelated input estimates is equivalent to the Pythagorean Theorem: $u_c^2(y) = u_1^2(y) + u_2^2(y)$.

6.4.12 Fig. 3 applies the same analogy in three dimensions for a measurement equation $y = f(x_1, x_2, x_3)$ with three inputs. Here the three uncertainty components are identified with the length, width, and height of a box, and the combined standard uncertainty is identified with the box's diagonal. In this case, $u_c^2(y) = u_1^2(y) + u_2^2(y) + u_3^2(y)$.

6.5 *Correlations:*

6.5.1 When input estimates may be correlated with each other, the complete law of propagation of uncertainty is written as follows:

$$u_c(y) = \sqrt{\sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \frac{\partial f}{\partial x_i}\frac{\partial f}{\partial x_j} u(x_i, x_j)} \quad (13)$$

In this equation, $u(x_i, x_j)$ denotes the estimated covariance of input estimates x_i and x_j. Note that $u(x_i, x_j) = u(x_j, x_i)$ and $u(x_i, x_i) = u^2(x_i)$.

6.5.2 The covariance $u(x_i, x_j)$ can also be written as:

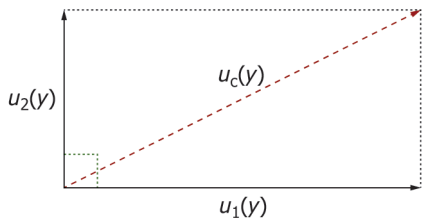

FIG. 2 Combining Two Uncertainty Components

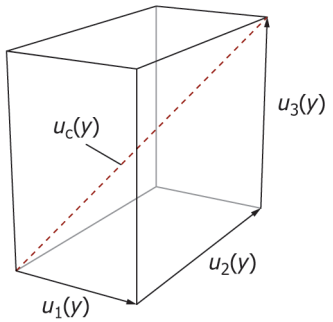

FIG. 3 Combining Three Uncertainty Components

$$u(x_i, x_j) = r(x_i, x_j)\, u(x_i)\, u(x_j) \quad (14)$$

where $r(x_i, x_j)$ denotes the estimated *correlation coefficient* of x_i and x_j:

$$r(x_i, x_j) = \frac{u(x_i, x_j)}{u(x_i)\, u(x_j)} \quad (15)$$

The correlation coefficient is always a dimensionless real number between −1 and +1.

NOTE 5—The input estimates x_i and x_j are correlated if $r(x_i, x_j) \neq 0$ and uncorrelated if $r(x_i, x_j) = 0$. The correlation is strong if $|r(x_i, x_j)|$ is near 1 and weak if it is near 0.

6.5.3 Typically, few inputs in a radiochemical measurement are significantly correlated and usually only when they are calculated from the same data. Common examples include calibration parameters, especially when the calibration involves a multi-parameter curve or when calibrations for two radionuclides are based on one standard solution (for example, ^{90}Sr and ^{90}Y calibrations using the same ^{90}Sr standard, as described in X5.3). Another common example is a correlation between the counting efficiency and the chemical yield, as described in 6.16.

6.5.4 When two inputs x_i and x_j are correlated only because they are calculated from other variables $w_1, w_2, \ldots, w_m$, the covariance $u(x_i, x_j)$ may be calculated as described below in 6.5.8. Alternatively, one may recast the measurement equation $y = f(x_1, x_2, \ldots, x_N)$, replacing x_i and x_j by the expressions used to calculate them, thereby eliminating the correlated inputs x_i and x_j from the equation and including new inputs $w_1, w_2, \ldots, w_m$, as shown below:

$$y = f(x_1, \ldots, x_{i-1}, x_{i+1}, \ldots, x_{j-1}, x_{j+1}, \ldots, x_N, w_1, \ldots, w_m) \quad (16)$$

6.5.5 To evaluate the covariance of two input quantities experimentally, see 6.3.8.

6.5.6 Generally, one estimates the covariance of two inputs only when there is a reason to suspect it may be nonzero. One may suspect a correlation whenever two inputs are measured using the same devices, or using different devices that are affected by the same influence quantities, such as ambient temperature, pressure, and humidity. Even when a correlation exists, if the uncertainty components generated by the two inputs are both small, the effect of the correlation is necessarily small, too, and might be ignored.

6.5.7 Fig. 2 graphically illustrated the propagation of uncertainty for two *uncorrelated* input estimates by analogy with the Pythagorean Theorem. Fig. 4 extends the geometric analogy to

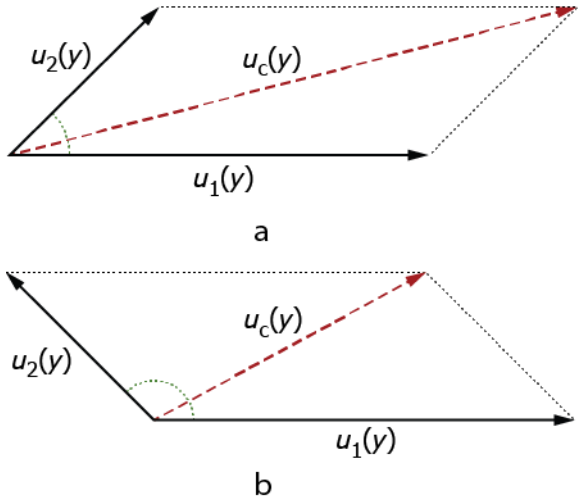

FIG. 4 Combining Uncertainties of Two Correlated Inputs

cases where the two input estimates are correlated. A correlation transforms the rectangle of Fig. 2 into a parallelogram with acute and obtuse angles, as shown. For either of the parallelograms in Fig. 4, the cosine of the indicated angle has the same absolute value as the correlation coefficient $r(x_1, x_2)$, with a sign that depends on whether the correlation increases the total uncertainty (a, positive cosine) or decreases it (b, negative cosine).

6.5.8 The covariance of two output estimates y and z calculated from input estimates $x_1, x_2, \ldots, x_N$ can be calculated using a formula similar to the law of propagation of uncertainty. Let $y=f(x_1,x_2,\ldots,x_N)$ and $z=g(x_1,x_2,\ldots,x_N)$. Then:

$$u(y,z) = \sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\partial f}{\partial x_i}\frac{\partial g}{\partial x_j}u(x_i,x_j) \tag{17}$$

If $x_1, x_2, \ldots,$ and x_N are uncorrelated, the preceding equation reduces to:

$$u(y,z) = \sum_{i=1}^{N}\frac{\partial f}{\partial x_i}\frac{\partial g}{\partial x_i}u^2(x_i) \tag{18}$$

Example—Suppose two sources are counted separately using a liquid scintillation counter and the results are background-corrected using the same background estimate. If the two gross count rates are R_{S1} and R_{S2} and the background count rate is R_B, the net count rates are given by $R_{N1} = R_{S1} - R_B$ and $R_{N2} = R_{S2} - R_B$. Since the variable R_B appears in both expressions, its uncertainty generates a covariance for R_{N1} and R_{N2}.

$$\begin{aligned} u(R_{N1},R_{N2}) &= \frac{\partial R_{N1}}{\partial R_B}\frac{\partial R_{N2}}{\partial R_B}u^2(R_B) \\ &= (-1)(-1)u^2(R_B) \\ &= u^2(R_B) \end{aligned} \tag{19}$$

6.5.9 The covariance of two calibration parameters calculated by least squares should be determined as part of the least-squares analysis. The method of weighted least squares provides not only a solution vector but also the estimated covariance matrix for the solution. The diagonal entries of this matrix are the variances of the estimated parameters, and the off-diagonal entries are the covariances.

6.5.10 The covariance of any pair of parameters may be divided by the product of the two parameters' uncertainties to obtain the estimated correlation coefficient, which is generally more convenient for record-keeping.

6.5.11 See X5.3 for more examples of the use of Eq 18.

6.6 *Alternatives for Uncertainty Propagation:*

6.6.1 It is often possible to implement Eq 10 without explicit calculation of derivatives using only the rules of uncertainty propagation for sums, differences, products, and quotients. Uncertainty propagation for sums and differences follows the pattern:

$$u_c(x_1 \pm x_2 \pm \cdots \pm x_n) = \sqrt{u^2(x_1)+u^2(x_2)+\cdots+u^2(x_n)} \tag{20}$$

6.6.2 More generally, if the variables x_i are multiplied by any constants a_i, the pattern becomes:

$$\begin{aligned} &u_c(a_1x_1+a_2x_2+\cdots+a_nx_n) = \\ &\sqrt{a_1^2u^2(x_1)+a_2^2u^2(x_2)+\cdots+a_n^2u^2(x_n)} \end{aligned} \tag{21}$$

NOTE 6—Eq 21 may be derived from the fact that:

$$\frac{\partial}{\partial x_i}(a_1x_1+a_2x_2+\cdots+a_nx_n) = a_i \tag{22}$$

6.6.3 For products and quotients, the pattern for uncertainty propagation is:

$$\begin{aligned} u_c\left(\frac{x_1x_2\ldots x_n}{w_1w_2\ldots w_m}\right) &= \left|\frac{x_1x_2\ldots x_n}{w_1w_2\ldots w_m}\right| \\ &\times\sqrt{\frac{u^2(x_1)}{x_1^2}+\cdots+\frac{u^2(x_n)}{x_n^2}+\frac{u^2(w_1)}{w_1^2}+\cdots+\frac{u^2(w_m)}{w_m^2}} \end{aligned} \tag{23}$$

provided that none of the factors x_i or w_j is zero. One may also rewrite Eq 23 in terms of relative variances:

$$\begin{aligned} u_{rel}^2\left(\frac{x_1x_2\ldots x_n}{w_1w_2\ldots w_m}\right) &= u_{rel}^2(x_1)+\cdots+u_{rel}^2(x_n) \\ &+u_{rel}^2(w_1)+\cdots+u_{rel}^2(w_m) \end{aligned} \tag{24}$$

where $u_{rel}(x_i)$ denotes the relative standard uncertainty, $u(x_i)/|x_i|$.

NOTE 7—Eq 23 may be derived from the fact that if $y=(x_1x_2\ldots x_n)/(w_1w_2\ldots w_m)$, where none of the factors is zero, then:

$$\frac{\partial y}{\partial x_i} = \frac{x_1\ldots x_{i-1}x_{i+1}\ldots x_n}{w_1w_2\ldots w_m} = \frac{y}{x_i} \tag{25}$$

and

$$\frac{\partial y}{\partial w_j} = -\frac{x_1x_2\ldots x_n}{w_1\ldots w_j^2\ldots w_m} = -\frac{y}{w_j} \tag{26}$$

6.6.4 If some of the x_i may be zero, Eq 23 must be rearranged to avoid division by those factors. For example, if x_1 could be zero, one might write either:

$$\begin{aligned} u_c\left(\frac{x_1x_2\ldots x_n}{w_1w_2\ldots w_m}\right) = \Bigg[&\left(\frac{x_2x_3\ldots x_n}{w_1w_2\ldots w_m}\right)^2u^2(x_1) \\ &+\left(\frac{x_1x_2\ldots x_n}{w_1w_2\ldots w_m}\right)^2\left(\frac{u^2(x_2)}{x_2^2}+\cdots+\frac{u^2(x_n)}{x_n^2}\right. \\ &\left.+\frac{u^2(w_1)}{w_1^2}+\cdots+\frac{u^2(w_m)}{w_m^2}\right)\Bigg]^{1/2} \end{aligned} \tag{27}$$

or

$$u_c\left(\frac{x_1x_2\ldots x_n}{w_1w_2\ldots w_m}\right) = \left|\frac{x_2x_3\ldots x_n}{w_1w_2\ldots w_m}\right| \times \sqrt{u^2(x_1)+x_1^2\left(\frac{u^2(x_2)}{x_2^2}+\cdots+\frac{u^2(x_n)}{x_n^2}+\frac{u^2(w_1)}{w_1^2}+\cdots+\frac{u^2(w_m)}{w_m^2}\right)} \quad (28)$$

The last two equations are equivalent to Eq 23 when all the factors are nonzero, but both are still valid if x_1 happens to be zero. For a less abstract example, see Eq 39 in 6.11.2, where the uncertainty equation is written to avoid division by the variable R_N.

6.6.5 More generally, if $p_1, p_2, \ldots, p_n$ are any exponents, not necessarily ± 1, and if none of the factors x_i is zero:

$$u_c(x_1^{p_1}x_2^{p_2}\ldots x_n^{p_n}) = \left|x_1^{p_1}x_2^{p_2}\ldots x_n^{p_n}\right| \times \sqrt{p_1^2\frac{u^2(x_1)}{x_1^2}+p_2^2\frac{u^2(x_2)}{x_2^2}+\cdots+p_n^2\frac{u^2(x_n)}{x_n^2}} \quad (29)$$

In terms of relative variances:

$$u_{rel}^2(x_1^{p_1}x_2^{p_2}\ldots x_n^{p_n}) = p_1^2u_{rel}^2(x_1)+p_2^2u_{rel}^2(x_2)+\cdots+p_n^2u_{rel}^2(x_n) \quad (30)$$

6.6.6 These simplified rules do not apply if the same input quantity appears more than once in the expression whose uncertainty is being evaluated. For example, the variance of $x + x$ is not $u^2(x) + u^2(x)$, or $2u^2(x)$, as one might infer incorrectly from Eq 20; it actually equals $u_c^2(2x)$, or $4u^2(x)$, as implied by Eq 21. When a variable appears more than once, it may be possible to recast the expression algebraically so that each variable appears only once, and the simplified rules can still be used. However, in some cases algebra fails and calculus is needed.

6.6.7 For measurement functions with more than a few input quantities, an explicit expression for the combined standard uncertainty can become quite complex, even using the rules described above. A number of software applications have been developed and are available to assist in reliably developing, testing, and documenting uncertainty models.

6.6.8 Other options for calculating the combined standard uncertainty without calculus often involve approximations for the sensitivity coefficients. For $i = 1, 2, \ldots, N$, the sensitivity coefficient $\partial f/\partial x_i$ may be approximated by:

$$\frac{\partial f}{\partial x_i} \approx \frac{1}{2u(x_i)}\left[f(x_1,\ldots,x_i+u(x_i),\ldots,x_N) - f(x_1,\ldots,x_i-u(x_i),\ldots,x_N)\right] \quad (31)$$

Recognizing this fact, the GUM allows the approximation:

$$u_c(y) \approx \sqrt{\sum_{i=1}^{N} Z_i^2} \quad (32)$$

where:

$$Z_i = \frac{1}{2}\left[f(x_1,\ldots,x_i+u(x_i),\ldots,x_N) - f(x_1,\ldots,x_i-u(x_i),\ldots,x_N)\right] \quad (33)$$

6.6.9 The *Kragten spreadsheet method* for propagating uncertainty (**4**) is based on a similar one-sided approximation of each sensitivity coefficient:

$$u_c(y) \approx \sqrt{\sum_{i=1}^{N} D_i^2} \quad (34)$$

where:

$$D_i = f(x_1,\ldots,\ x_i+u(x_i),\ \ldots,x_N) - f(x_1,\ldots,x_N) \quad (35)$$

6.6.10 Another method for uncertainty propagation is Monte Carlo simulation, described in JCGM 101. The Monte Carlo method evaluates both the output estimate y and its standard uncertainty $u(y)$ by analyzing the distribution of results produced in many trials of a computer simulation of the measurement. In each trial, the algorithm generates pseudo-random values for the input quantities X_i by sampling from their estimated or assumed distributions, and uses the measurement function $f(x_1, x_2, \ldots, x_N)$ to calculate a value for the output quantity Y. The output estimate y and its standard uncertainty $u(y)$ are then given by the average and experimental standard deviation of all the trial results. For details of the method and a discussion of its advantages and disadvantages in relation to the standard GUM approach, see JCGM 101.

6.7 *Calculating Coverage Factors:*

6.7.1 As discussed earlier, the combined standard uncertainty $u_c(y)$ may be multiplied by a coverage factor k to obtain an expanded uncertainty $U = k \cdot u_c(y)$ such that the coverage interval from $y - U$ to $y + U$ is believed to contain the true value of the measurand with high probability. The coverage factor most commonly used in reports of radiochemical measurement results is $k = 2$, which is usually assumed to produce a coverage interval with approximately 95 % coverage probability. For some purposes, especially internal laboratory quality control, the coverage factor $k = 3$ is often used. The coverage probability at $k = 3$ is assumed to be more than 99 %, so that the interval from $y - U$ to $y + U$ should "almost always" contain the true value of the measurand.

6.7.2 If the distribution of the measurement result y is normal (Gaussian) and if its combined standard uncertainty $u_c(y)$ is a sufficiently accurate estimate of the standard deviation of that distribution, then the coverage factor k_p that provides a specified coverage probability p is approximated by the $(1+p)/2$-quantile of the standard normal distribution, $z_{(1+p)/2}$. Table 2 lists several values of k_p based on this approximation.

6.7.3 Laboratories often use the approximation described above by default regardless of whether the uncertainty is well-known. In most cases, the combined standard uncertainty $u_c(y)$ is not known well enough to justify retaining more than two significant figures in the value of k_p.

6.7.4 As discussed in 6.3.13, one may calculate the number of degrees of freedom ν_i for the Type A or Type B standard uncertainty $u(x_i)$ of each input estimate. Given the degrees of freedom ν_i for all the input estimates, it is possible to calculate the *effective degrees of freedom*, ν_{eff}, for the combined standard uncertainty and to use ν_{eff} to estimate a somewhat better coverage factor k_p for a specified coverage probability p.

TABLE 2 Coverage Factors: Well-Characterized Uncertainty

p	$(1+p)/2$	$k_p = z_{(1+p)/2}$
95.0 %	0.975	2.0
99.0 %	0.995	2.6
99.5 %	0.9975	2.8
99.7 %	0.9985	3.0

6.7.5 Assuming that none of the input estimates are correlated with each other and that the combined standard uncertainty $u_c(y)$ is not dominated either by a Type A uncertainty component with only a few degrees of freedom or by a Type B component based on a distribution that is very different from a normal distribution, one may use the *Welch-Satterthwaite formula*, shown below, to calculate the effective degrees of freedom for $u_c(y)$.

$$\nu_{eff} = \frac{u_c^4(y)}{\sum_{i=1}^{N} \frac{u_i^4(y)}{\nu_i}} \quad (36)$$

Note that if the number of Type B degrees of freedom ν_i for an input estimate x_i is infinite, the i^{th} term of the sum in the denominator of Eq 36 is zero and should be omitted.

6.7.6 Given ν_{eff}, estimate the coverage factor k_p by the $(1+p)/2$-quantile of the t-distribution with ν_{eff} degrees of freedom.

$$k_p = t_{(1+p)/2}(\nu_{eff}) \quad (37)$$

Round k_p to either 2 or 3 figures. Table 3 provides examples of k_p calculated in this manner.

NOTE 8—The calculated value of ν_{eff} is generally not an integer. Some software packages may be able to calculate the quantile $t_{(1+p)/2}(\nu_{eff})$ for non-integral degrees of freedom. When such software is unavailable, either interpolate between values of t for integral degrees of freedom or truncate ν_{eff} to a whole integer.

6.8 *Reporting the Uncertainty:*

6.8.1 The report of the measurement should indicate whether the uncertainty is the combined standard uncertainty or an expanded uncertainty. For an expanded uncertainty, the report should state the coverage factor k and the approximate coverage probability p. The report should also include a statement if the stated uncertainty does not represent the total uncertainty of the measurement—as for example, if it represents only the counting uncertainty.

6.8.2 In most cases, the uncertainty of a measured value is expressed in the same measurement unit as the value itself. One may also report the relative uncertainty as a percentage, provided that the measured value is nonzero and especially if its uncertainty is relatively small, as for example when analyzing high-activity samples, spikes, or reference materials.

6.8.3 *Rounding:*

6.8.3.1 For most purposes, the reported uncertainty should be rounded to either one or two figures and the measured value should then be rounded to the same power of 10 as the uncertainty. A traditional rule is to round the uncertainty to one figure unless the resulting figure is a 1, in which case the uncertainty is rounded to two figures. A simpler rule, recommended by ANSI N42.23 and MARLAP (**2**), is to round the uncertainty to two figures in all cases. This simpler rule is also recommended by the NIST Weights and Measures Division in Good Laboratory Practice (**5**) and is used at the "NIST Reference on Constants, Units, and Uncertainty" (**6**).

6.8.3.2 Never round the reported result of a measurement to a power of 10 that is larger than the combined standard uncertainty. Such rounding would introduce significant additional uncertainty, which might dominate all other components.

6.8.3.3 Do not round intermediate results of calculations unnecessarily. Round only final results and their uncertainties as described above.

6.8.4 *Shorthand Formats:*

6.8.4.1 When the laboratory reports a measurement result, it may present the measured value and the uncertainty as distinct, clearly identified items—for example, in different columns of a table. Alternatively, it may present the value and its uncertainty in a single expression using one of the shorthand formats described below.

6.8.4.2 The most common shorthand format for reporting a result with its combined standard uncertainty places the digits of the rounded uncertainty in parentheses immediately after the final digits of the rounded measured value. For example, a value of 0.124 Bq/g with combined standard uncertainty 0.037 Bq/g is represented by 0.124(37) Bq/g. When scientific notation is used, the expression becomes $1.24(37) \times 10^{-1}$ Bq/g. For examples of the use of this format, see the "NIST Reference on Constants, Units, and Uncertainty" (**6**).

6.8.4.3 It is also possible to put the entire expression for the combined standard uncertainty inside parentheses, as in 0.124(0.037) Bq/g, although this format is less commonly used.

6.8.4.4 The shorthand format for reporting a result with its expanded uncertainty places the symbol ± between the numerical measured value and uncertainty. When the unit of measurement is included, the entire expression is placed in parentheses and followed by the unit symbol, as in (0.124 ± 0.074) Bq/g. When scientific notation is used, this expression becomes $(1.24 \pm 0.74) \times 10^{-1}$ Bq/g.

6.8.4.5 Although one may encounter other uncertainty-reporting conventions—for example, reporting the digits of the combined standard uncertainty without parentheses—it is recommended that laboratories use one of the standard conventions described above.

6.8.4.6 Shorthand formats can be used even when the rounded result is zero.

Example—A measured value of 0.000124 Bq/g with combined standard uncertainty 0.037 Bq/g could be expressed as 0.000(37) Bq/g or $0.0(37) \times 10^{-2}$ Bq/g. Applying a coverage factor $k = 2$, the same result with its expanded uncertainty would be (0.000 ± 0.074) Bq/g or $(0.0 \pm 7.4) \times 10^{-2}$ Bq/g. In this case, since the measured value rounds to zero, the magnitude of the uncertainty determines the power of 10 used for scientific notation.

6.9 *Quality Control:*

TABLE 3 Coverage Factors (Examples)

	$k_p = t_{(1+p)/2}(\nu_{eff})$			
ν_{eff}	p = 95.0%	99.0%	99.5%	99.7%
5	2.57	4.03	4.77	5.38
10	2.23	3.17	3.58	3.89
15	2.13	2.95	3.29	3.54
20	2.09	2.85	3.15	3.38
25	2.06	2.79	3.08	3.29
30	2.04	2.75	3.03	3.23
50	2.01	2.68	2.94	3.12
100	1.98	2.63	2.87	3.04
∞	1.96	2.58	2.81	2.97

6.9.1 As mentioned earlier, statistical control of the measurement process is a prerequisite for meaningful uncertainty evaluations. The rigor of the quality control (QC) regimen for both instruments and analytical measurements should be appropriate for the level of measurement uncertainty required. QC can also support uncertainty evaluations as discussed below.

6.9.2 *As a source of data*—Routine QC, especially instrument QC, generates large amounts of data that can often be used to evaluate uncertainty components. See 6.15.4, X2.2, X6.1, and X6.2 for example. Analytical QC data (from spikes, replicates, and blanks) may be used to evaluate some uncertainty components, as described in 6.19. In fact, it is rather common for chemical (but not radiochemical) testing laboratories to base uncertainty evaluations for sample measurements almost entirely on analytical QC data.

6.9.3 *As a check of uncertainty estimates*—QC acceptance criteria should be based either on the estimated uncertainties of the measurement results or on the same models, tolerances, and assumptions used for the uncertainties of measurement results. In this way, the quality control serves as a routine check of the uncertainty estimates. For example, if it is assumed that the response of an instrument can vary randomly, the same random variation should be reflected in both the sample measurement uncertainties and the acceptance limits for the instrument's routine QC checks. See also the description of the normalized absolute difference (*NAD*) in 6.19.8, which is defined explicitly in terms of the uncertainties of sample measurements.

6.9.4 Radiochemistry laboratories commonly evaluate analytical QC results using uncertainty-based statistics. Unfortunately, there is as yet no commonly accepted terminology for these statistics. The terms *normalized difference*, *normalized absolute difference*, *relative difference*, *duplicate error ratio*, *replicate error ratio*, *zeta score*, and *Z score* have all been used for similar concepts. In the context of analytical QC, each of these terms denotes a statistic based either on the ratio of a measured value to its combined standard uncertainty (for a blank result) or on the ratio of the difference between two measured values to the combined standard uncertainty of that difference (for duplicate and spike results).

NOTE 9—In the context of proficiency testing, the term *zeta score* is the common term for this type of uncertainty-based statistic, while *Z score* denotes a somewhat different statistic, equal to the difference between a measured value and an accepted value divided by the acceptable standard deviation. The term E_n *number* (where n is a small positive number) denotes a statistic similar to a zeta score but calculated using expanded uncertainties ($k = n$) rather than combined standard uncertainties ($k = 1$).

6.10 *Practical Significance of Uncertainty Components:*

6.10.1 It is impossible to identify, evaluate, and propagate every possible component of the total uncertainty. Fortunately, it is not necessary to do so. This guide assumes that if uncertainty components accounting for 98 % of the total uncertainty are evaluated and propagated, any components that are left over *may* be considered negligible. Calculations based on this assumption show how small a component or combination of components must be to be safely neglected.

NOTE 10—The choice of 98 % is based on calculations of coverage probabilities for expanded uncertainties with coverage factors between 2 and 3. If results are normally distributed, then underestimating the standard deviation of the distribution by 2 % decreases the coverage probability at $k = 2$ from 95.45 % to 94.76 %, and it decreases the coverage probability at $k = 3$ from 99.73 % to 99.64 %. Coverage calculations based on t-distributions produce similar results.

6.10.2 A consequence of the fact that uncertainty components add "in quadrature" and not linearly is that small components can make tiny contributions to the combined uncertainty. For this reason, the laboratory should focus on identifying and quantifying the largest components of uncertainty first. The biggest improvements in the quality of a "total" uncertainty evaluation are likely to come from examinations of relatively few components.

6.10.3 For illustration, consider Table 4, which shows the effects of removing or adding a hypothetical uncertainty component $u_i(y)$ generated by an input estimate x_i that is not correlated with other input estimates. The first column represents the magnitude of $u_i(y)$ relative to the combined standard uncertainty $u_c(y)$. The second column shows the effect of removing the component $u_i(y)$ from $u_c(y)$, while the third column shows the effect of adding a component of size $u_i(y)$ to $u_c(y)$. Note that all the percentages shown are relative to $u_c(y)$, not to y itself. So, for example, a value of 10 % in the first column does not indicate a relative standard uncertainty of 10 %; instead, it represents an uncertainty component whose size is 10 % of $u_c(y)$.

NOTE 11—If the input estimate x_i is strongly correlated with other input estimates, Table 4 is not applicable. In such cases, the effect of a component together with its correlations may be much larger or much smaller than indicated.

6.10.4 Table 4 shows that by the criteria for significance stated above, a single uncertainty component $u_i(y)$ whose size does not exceed 20 % of the combined standard uncertainty may be considered negligible, since it contributes at most 2 % of the total uncertainty. So, for example, if the relative combined standard uncertainty is always at least 5 %, a single uncertainty component of only 1 % or less might reasonably be neglected.

6.10.5 Fig. 5 applies the geometric analogy of 6.4.11 to illustrate the 20 % rule. In the figure, the length of the $u_2(y)$ leg of the right triangle is 20 % of the length of the hypotenuse, $u_c(y)$. The contribution of $u_2(y)$ to $u_c(y)$ is indicated by the 2 % difference in lengths between the hypotenuse and the $u_1(y)$ leg.

6.10.6 The 20 % rule as stated above applies only to a judgment made about a single uncertainty component when all other nontrivial components are included in the total uncertainty. Components that are individually negligible by the 20 % rule may be collectively significant when considered together.

TABLE 4 Effect of Component $u_i(y)$ on $u_c(y)$

$\frac{u_i(y)}{u_c(y)}$	$\frac{\sqrt{u_c^2(y) - u_i^2(y)}}{u_c(y)}$	$\frac{\sqrt{u_c^2(y) + u_i^2(y)}}{u_c(y)}$
30 %	95.4 %	104.4 %
25 %	96.8 %	103.1 %
20 %	**98.0 %**	**102.0 %**
15 %	98.9 %	101.1 %
10 %	99.5 %	100.5 %
5 %	99.9 %	100.1 %

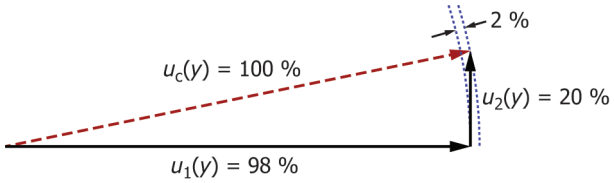

FIG. 5 The 20 % Rule

The combined effect of n components of similar magnitude on the total uncertainty is comparable to that of a single component that is $\sqrt{n}$ times as large. For example, if there are four uncertainty components, each representing ~15 % of $u_c(y)$, their combined contribution to $u_c(y)$ is the same as that of a single component that is twice as large (~30 % of $u_c(y)$), making them collectively significant by the criteria stated above. Omitting all four of these components would underestimate the total uncertainty.

6.10.7 The judgment of whether uncertainty components are negligible in a particular measurement process requires consideration of all likely measurement scenarios. A component that is negligible in the analysis of one sample may be significant in the analysis of another. For example, when very low activities in environmental samples are measured, counting uncertainty often dominates the uncertainty and many other components can be relatively insignificant. When analyzing high-activity samples, other uncertainty components may dominate.

6.10.8 If an uncertainty component is easily evaluated and propagated, it should be included in the total regardless of whether it is negligible by the stated criteria, especially if its size exceeds 5 % of the combined standard uncertainty.

6.11 *The Canonical Measurement Model for Radiochemistry:*

6.11.1 In many cases, the measurement model for a radiochemical measurement can be reduced to the form:

$$AC = \frac{R_N}{V \cdot Y \cdot \varepsilon \cdot DF \cdot I} \tag{38}$$

where:

AC = the analyte activity concentration,
R_N = the net count rate for the analyte,
V = the aliquot size (or volume),
Y = the chemical yield,
ε = the counting efficiency,
DF = the analyte decay factor, and
I = the analyte's radiation emission probability (or intensity).

NOTE 12—In this equation, four of the input estimates, R_N, Y, ε, and DF, are actually output estimates from other measurement functions, and their standard uncertainties are the combined standard uncertainties obtained by uncertainty propagation.

6.11.2 The expression in Eq 38 involves only products and quotients of factors, which suggests the use of Eq 23 to propagate the uncertainties. However, since the factor R_N may be zero, the uncertainty equation in this case takes the following form to avoid a potentially fatal division by R_N:

$$u_c(AC) = \left[\frac{u^2(R_N)}{(V \cdot Y \cdot \varepsilon \cdot DF \cdot I)^2} + AC^2 \left(\frac{u^2(V)}{V^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(DF)}{DF^2} + \frac{u^2(I)}{I^2} + \cdots \right) \right]^{1/2} \tag{39}$$

Here the ellipsis indicates the possibility of additional uncertainty terms, such as terms for subsampling uncertainty or correlations between pairs of input estimates.

NOTE 13—When the model includes both a yield Y and an efficiency ε, these two variables are often (negatively) correlated, as described in 6.16, in which case the ellipsis in Eq 39 includes the additional (negative) term $2u(Y, \varepsilon) / (Y \cdot \varepsilon)$.

6.11.3 The uncertainty equation as written above always gives a nonnegative value for the uncertainty $u_c(AC)$. When $R_N = 0$, the calculated value of AC is also zero. In this case, it is important to ensure that the estimated variance $u^2(R_N)$ is positive to avoid calculating $u_c(AC) = 0$ (see 6.12.10).

6.12 *Counting Uncertainty:*

6.12.1 The term *counting uncertainty* (traditionally called "counting error") refers to the uncertainty of a measured result due to the inherent variability of counting random events, often called "counting statistics." In the radiation laboratory, *counting uncertainty* is synonymous with the uncertainty due to the variability of the number of pulses registered by a radiation detector. These pulses, or *counts*, vary because of the randomness of radioactive decay and radiation detection, and possibly because of other effects related to the discrete nature of the analyte atoms.

6.12.2 The total variability of the observed counts may include variability due to causes other than counting statistics, as described for example in 6.14, X6.1, and X6.2. Such "excess" variability is ordinarily not included in the counting uncertainty and must be evaluated and included as a separate component of the total measurement uncertainty.

6.12.3 Radiation counts observed in a fixed time period are often modeled using either a Poisson distribution or a binomial distribution. Both models presume that a single decaying atom can produce at most one count and that the counts produced by different atoms are independent of each other. The Poisson model, which is more convenient for calculations, presumes further that the probability that any single atom will decay and produce a count is negligibly small, and therefore that the only reason statistically significant counts are ever seen is that the number of atoms available to decay may be huge. The common assumption of Poisson counting statistics in most radiochemical methods is probably valid much more often than not, although 6.22 provides examples where both the Poisson and binomial models fail.

6.12.4 A binomial distribution is specified by two parameters n and p, where n is a positive integer and p is a probability between 0 and 1. When the distribution is used as a model for radiation counts, n is the total number of analyte atoms in the sample or aliquot at the reference date and p is the probability that any particular atom generates a count. When p is small, the binomial distribution is approximated by a Poisson distribution with a single parameter $\lambda = np$. In radiation counting, p is usually so tiny that the Poisson approximation is excellent. Exceptions to this rule can occur when the entire sample or a

large fraction is analyzed and counted for a time that is long compared to the half-life. Because of the rarity of such exceptions, the following guidance assumes Poisson counting except as noted in 6.13 and 6.22.

6.12.5 Examples of probability mass functions for a binomial distribution and a Poisson distribution are shown in Figs. 6 and 7.

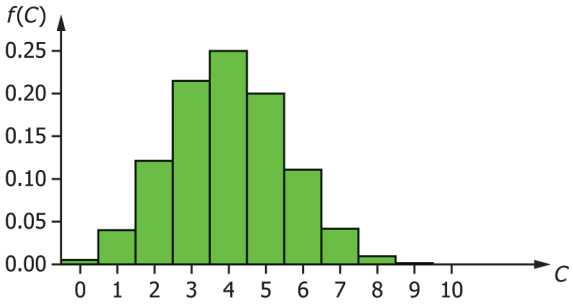

FIG. 6 Binomial Distribution (n = 10, p = 0.4)

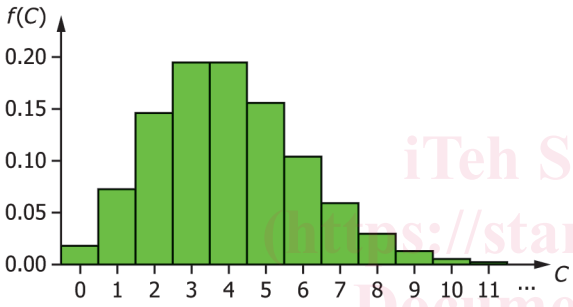

FIG. 7 Poisson Distribution (λ = 4)

Note that there are only finitely many possible values for the binomial distribution ($0 \le C \le 10$ in this example), but the Poisson distribution includes all nonnegative integers. Although the two distributions have the same mean ($\lambda = np$), they are noticeably different because of the large size of the binomial parameter p.

6.12.6 A salient feature of any Poisson distribution is the equality of its mean and variance. This equality allows one to estimate both the mean and variance from a single observation C and to estimate the standard deviation—or the standard uncertainty—by taking the square root of C. Thus:

$$u(C) = \sqrt{C} \tag{40}$$

6.12.7 Since the mean and variance of a Poisson distribution are equal, the variance-to-mean ratio, also called the *index of dispersion*, equals 1. If C instead has a binomial distribution with parameters n and p, the variance-to-mean ratio is $1 - p$, and the standard uncertainty $u(C)$ is less than $\sqrt{C}$. So, in the rare scenarios in which radiation counts are better modeled by a binomial distribution, the Poisson approximation tends to overestimate the counting uncertainty.

6.12.8 The net count rate for an analysis is typically given by:

$$R_N = R_S - R_B = \frac{C_S}{t_S} - \frac{C_B}{t_B} \tag{41}$$

where:

R_N = the net count rate,
R_S = the gross sample count rate,
R_B = the background or blank count rate,
C_S = the number of gross sample counts,
C_B = the number of background or blank counts,
t_S = the sample count time (live time), and
t_B = the background/blank count time.

Eq 41 is linear in the variables C_S and C_B. So, provided the count times are known with negligible uncertainty, Eq 21 implies:

$$u^2(R_N) = u^2\left(\frac{C_S}{t_S} - \frac{C_B}{t_B}\right) = \frac{u^2(C_S)}{t_S^2} + \frac{u^2(C_B)}{t_B^2} \tag{42}$$

Then, assuming Poisson uncertainties for C_S and C_B:

$$u^2(R_N) = \frac{C_S}{t_S^2} + \frac{C_B}{t_B^2} = \frac{R_S}{t_S} + \frac{R_B}{t_B} \tag{43}$$

6.12.9 Some counting systems provide the option of counting until a preset number of counts are registered. With this option, the count time t is a random variable. The assumptions that imply a Poisson distribution for a variable count C suggest a gamma distribution for the variable count time t when the count rate is steady and C is fixed. The standard uncertainty of a count rate $R = C / t$ can be estimated by R/t regardless of whether C or t is varying. So, Eq 43 remains valid.

6.12.10 When activity and background levels are low enough (for example, in some alpha-counting measurements, including alpha-particle spectrometry), it is possible to observe zero counts, $C = 0$, in which case Eq 40 gives the unrealistic estimate $u(C) = 0$. Whenever such low counts are possible, estimate the Poisson counting uncertainty instead by:

$$u(C) = \sqrt{C+1} \tag{44}$$

With the preceding equation, $u(C) = 1$ for $C = 0$, $u(C) = 1.4$ for $C = 1$, and so on. The variance of R_N is estimated now by:

$$\begin{aligned} u^2(R_N) &= \frac{C_S+1}{t_S^2} + \frac{C_B+1}{t_B^2} \\ &= \frac{R_S}{t_S} + \frac{R_B}{t_B} + \left(\frac{1}{t_S^2} + \frac{1}{t_B^2}\right) \end{aligned} \tag{45}$$

6.12.11 When evaluating the standard uncertainty of C as $u(C) = \sqrt{C}$, estimate the number of Type B degrees of freedom to be $2C$. When evaluating the uncertainty as $u(C) = \sqrt{C+1}$, estimate the number of degrees of freedom to be $2C + 2$. Note that the number of degrees of freedom associated with a Poisson estimate of counting uncertainty can be quite large, depending on the value of C. In fact, the Poisson estimate is the best available estimate of the uncertainty due to counting statistics in many common scenarios, regardless of C.

6.12.12 Although the counting uncertainty may often be the largest component of uncertainty, especially when environmental samples are analyzed, one should not simply assume that all other components are insignificant. In particular, the uncertainty due to subsampling heterogeneous solid material can be substantial, and uncertainties due to interferences, peak tailing, or non-stationary background may be significant when small activities are measured. Other uncertainty components may dominate when very high activities are measured.

6.13 *Dead Time and Pulse Pile-up:*

6.13.1 Uncorrected or incompletely corrected effects from dead time and pulse pile-up can produce deviations from Poisson counting statistics. These effects are usually significant only at high count rates.

6.13.2 If the effects of dead time and pile-up are significant but uncorrected, the observed real-time count rate is reduced and the variance of the total number of counts is less than the mean. Many counting systems apply automatic corrections for dead time, extending the total count time as necessary to achieve a specified live time. If the dead time and live time are estimated accurately, the number of observed counts C may still be assumed to follow a Poisson distribution.

6.13.3 Simple models for dead-time corrections tend to work best when the dead-time rate is low, producing best results when the rate is less than ~10 %. However, systems using the newest technologies to compensate for dead time and pulse pile-up may produce counts and live time estimates that are accurate enough to allow the assumption of Poisson counting statistics even at very high count rates. Pommé et al. (**7**) describe many of the relevant issues and technologies.

6.13.4 If the uncertainty of the live time t_S is known, it can be propagated by adding the term $R_S^2 u_{rel}^2(t_S)$ to the estimated variance $u^2(R_N)$, as shown in Eq 46.

$$u^2(R_N) = \frac{R_S}{t_S} + \frac{R_B}{t_B} + R_S^2 u_{rel}^2(t_S) \quad (46)$$

However, determining the uncertainty of t_S may be difficult. One should limit the dead-time rate to 10 % unless corrections for dead time and pile-up and the associated uncertainty models can be validated empirically at higher rates.

6.13.5 Specialized techniques such as "loss-free counting" or "zero dead-time" counting are needed to compensate for high dead-time and pile-up rates when the count rate varies significantly during the counting period—for example, because of rapidly decaying or ingrowing radionuclides. Live-time correction is generally inadequate in these situations. Even with the more advanced technologies, the counting statistics at high count rates are generally not Poisson.

6.14 *Background:*

6.14.1 In the preceding section, the number of background counts, C_B, is assumed to follow a Poisson law. In practice, the background may have short-term and long-term variability in excess of what is predicted by that model. To account for the additional variability, one may include an additional term ξ^2 in the expression for the variance $u^2(R_N)$:

$$u^2(R_N) = \frac{R_S}{t_S} + \frac{R_B}{t_B} + \xi^2 \quad (47)$$

or

$$u^2(R_N) = \frac{R_S}{t_S} + \frac{R_B}{t_B} + \left(\frac{1}{t_S^2} + \frac{1}{t_B^2}\right) + \xi^2 \quad (48)$$

The term ξ^2 has the dimension T^{-2} and its square root ξ has the dimension of a count rate, T^{-1}.

6.14.2 The value of the "excess" term can be estimated from historical background measurement data. If n consecutive background measurements have been made, one may estimate the excess variability using the equation:

$$\xi^2 \approx \frac{1}{n-1}\sum_{i=2}^{n}\left((R_i - R_{i-1})^2 - \left(\frac{R_{i-1}}{t_i} + \frac{R_i}{t_{i-1}}\right)\right) \quad (49)$$

where:

n = the number of background measurements,
R_i = the count rate observed in the i^{th} background measurement, for $i = 1$ to n, and
t_i = the count time for the i^{th} background measurement.

It is possible for the equation above to produce a negative estimate for ξ^2. If this happens, set $\xi^2 = 0$.

6.14.3 A large number of background measurements, n, may be needed to obtain a good estimate of ξ^2. If several instruments of the same type and model are in use and have similar histories, one might choose to pool background measurement data from all of them. Pooling the data is accomplished by calculating a sum like the one shown in Eq 49 for each instrument (without the division by $n - 1$), adding the sums together, and then dividing the total sum by the total number of terms, which equals the total number of measurements minus the number of instruments. See X6.1 for an example.

6.14.4 If the background varies cyclically, and if samples and backgrounds are routinely counted at different points of the cycle (for example, daytime versus nighttime or weekdays versus weekends), the background correction may be biased. Such situations can be avoided by better scheduling of measurements.

6.15 *Counting Efficiency:*

6.15.1 The uncertainty of the counting efficiency ε may have several components, including at least the uncertainties of the calibration standards and the counting uncertainties of the calibration measurements. There may also be uncertainties due to instability or drift of the instrument response and to geometry variations among sources. When the efficiency is obtained from a calibration curve, there may be significant uncertainty due to errors in empirical calibration models—for example, in gamma-ray spectrometry or in gas proportional counting with mass-attenuation corrections. Since calibration models and procedures vary, only general guidelines are provided here.

6.15.2 The uncertainty of the activity of a calibration standard should be stated on the accompanying certificate. There may also be uncertainty associated with the laboratory's preparation of calibration sources from purchased standards.

6.15.3 Counting uncertainties for calibration measurements may be evaluated in the manner described in 6.12.

6.15.4 Uncertainties due to instability of the instrument may be estimated from routine QC checks in a manner similar to that described in 6.14.2 for estimating background variability. For an example, see X6.2.

6.15.5 Uncertainties due to geometry variations may be estimated differently depending on the type of variation. The geometry of the calibration sources should match the geometries of sample test sources as well as possible. Differences may not only increase the uncertainty but may also lead to measurement bias. Variations in source position should be controlled as much as practical, but their effects may also be