

19 MEASUREMENT STATISTICS

19.1 Overview

This chapter discusses statistical principles and methods applicable to radioanalytical measurements, calibrations, data interpretation, and quality control.

Laboratory measurements always involve uncertainty, which must be considered when analytical results are used as part of a basis for making decisions. Every measured value obtained by a radioanalytical procedure should be accompanied by an explicit uncertainty estimate. One purpose of this chapter is to give users of radioanalytical data an understanding of the causes of measurement uncertainty and of the meaning of uncertainty statements in laboratory reports. The chapter also describes procedures which laboratory personnel use to estimate uncertainties.

The uncertainty associated with laboratory measurements is only a part of the total uncertainty that a data user must consider. Field sampling introduces other types of uncertainty, which are beyond the scope of this chapter.

Environmental radioactivity measurements may involve material containing very small amounts of the radionuclide of interest. Measurement uncertainty often makes it difficult to distinguish such small amounts from zero. An important performance characteristic of an analytical procedure is therefore its *detection capability*, which is usually expressed as the smallest concentration of analyte that can be reliably distinguished from zero. Effective project planning requires knowledge of the detection capabilities of the analytical procedures which will be or could be used. This chapter explains the performance measure, called the “minimum detectable concentration,” or in certain cases the “minimum detectable amount,” that is used to describe radioanalytical detection capabilities, as well as some proper and improper uses for it. The chapter also gives laboratory personnel methods for calculating the minimum detectable concentration.

Project planners also need to know the *quantification capability* of an analytical procedure, or its capability for precise measurement. The quantification capability is expressed as the smallest concentration of analyte that can be measured with a specified relative standard deviation. This chapter explains a performance measure called the “minimum quantifiable concentration,” which may be used to describe quantification capabilities.

The material in the chapter is arranged so that general information is presented first and the more technical information intended primarily for laboratory personnel is presented last. The general discussion in Sections 19.2 through 19.4 requires little previous knowledge of statistics on the part of the reader and involves no mathematical formulas. Section 19.2 in particular may be

33 skipped by those familiar with basic statistical concepts. The technical discussion in Sections
34 19.5 through 19.7 requires an understanding of basic algebra and at least some familiarity with
35 the fundamental concepts of probability and statistics. Attachments 19B–G are intended for tech-
36 nical specialists with stronger mathematical backgrounds. The footnotes also contain information
37 which may be skipped by most readers.

38 **19.2 Statistical Concepts and Terms**

39 **19.2.1 Basic Concepts**

40 Every laboratory measurement involves a measurement error. Methods for analyzing measure-
41 ment error are generally based on the theory of random variables. A *random variable* may be
42 thought of as the numerical outcome of an experiment, such as a laboratory measurement, which
43 produces varying results when repeated. In this document a random variable will most often be
44 the result of a measurement. Random variables will usually be denoted by upper-case letters.

45 Of primary importance in almost any discussion of a random variable is its *distribution*. The
46 distribution of a random variable X describes the possible values of X and their probabilities.
47 Although the word “distribution” has a precise meaning in probability theory, the term will be
48 used loosely in this document. Attachment 19A describes several types of distributions, including
49 the following:

- 50 • Normal (Gaussian) distributions
- 51 • Log-normal distributions
- 52 • Chi-square distributions
- 53 • Student’s t -distributions
- 54 • Rectangular, or uniform, distributions
- 55 • Trapezoidal distributions
- 56 • Exponential distributions
- 57 • Binomial distributions
- 58 • Poisson distributions

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

62 The distribution of X is uniquely determined by its *distribution function*, defined by $F(x) =$
63 $\Pr[X \leq x]$, where $\Pr[X \leq x]$ denotes the probability that X is less than or equal to x . If there is a
64 function $f(x)$ such that the probability of any event $a \leq X \leq b$ is equal to $\int_a^b f(x) dx$ (i.e., the area
65 under the curve $y = f(x)$ between $x = a$ and $x = b$), then X is a *continuous* random variable and $f(x)$
66 is a *probability density function* (pdf) for X . When X is continuous, the pdf uniquely describes its
67 distribution. A plot of the pdf is the most often used graphical illustration of the distribution (e.g.,
68 see Figures 19.1 and 19.2), because the height of the graph over a point x indicates the probabili-
69 ty that the value of X will be near x .

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

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

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

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

88 The mean is only one measure of the center of a distribution. Two others are the median and the
89 mode. The *median* of X is a value $x_{0.5}$ that splits the range of X into upper and lower portions
90 which are equally likely, or, more correctly, a value $x_{0.5}$ such that the probability that $X \leq x_{0.5}$ and
91 the probability that $X \geq x_{0.5}$ are both at least 0.5. The *mode* of X is its most likely value. Figure
92 19.1 shows the probability density function of a symmetric distribution, whose mean, median,
93 and mode coincide, and Figure 19.2 shows the pdf of an asymmetric distribution, whose mean,
94 median, and mode are distinct.

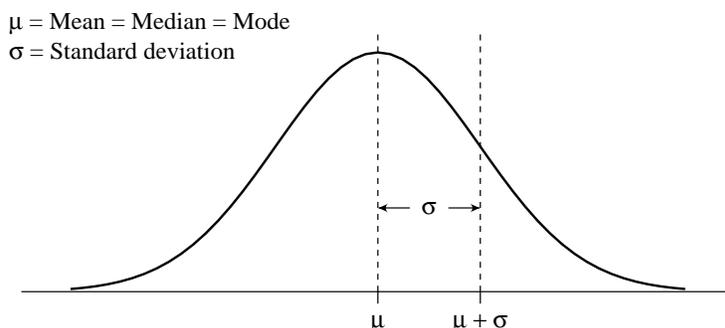


FIGURE 19.1 — A symmetric distribution

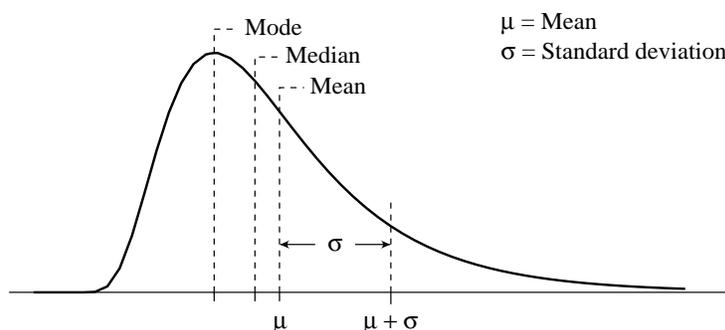


FIGURE 19.2 — An asymmetric distribution

95 For some distributions, the median or mode may not be unique. If there is a unique mode, the dis-
96 tribution is called *unimodal*; otherwise, it is called *multimodal*.

97 The median of X is also called a *quantile of order 0.5*, or a *0.5-quantile*. In general, if p is a num-
98 ber between 0 and 1, a p -quantile of X is a number x_p such that the probability that $X < x_p$ is at
99 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.

100 Sometimes the standard deviation of a nonnegative quantity is more meaningful when expressed
101 as a fraction of the mean. The *coefficient of variation*, or CV, is defined for this reason as the
102 standard deviation divided by the mean. The coefficient of variation is a dimensionless number,
103 which may be converted to a percentage. The term “relative standard deviation,” or RSD, is also

104 used. The term “relative variance” is sometimes used to mean the square of the relative standard
105 deviation.

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

112 Covariance, like variance, is somewhat nonintuitive because of its physical dimensions. Further-
113 more, a large value for the covariance of two variables X and Y does not necessarily indicate a
114 strong correlation between them. A measure of correlation must take into account not only the
115 covariance $\sigma_{X,Y}$, but also the standard deviations σ_X and σ_Y . The *correlation coefficient*, denoted
116 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
117 number between -1 and $+1$. The quantities X and Y are said to be strongly correlated when the
118 absolute value of their correlation coefficient is close to 1.

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

122 The lack of a correlation between two quantities X and Y is not a sufficient condition to guarantee
123 that two values $f(X)$ and $g(Y)$ calculated from them will also be uncorrelated. A stronger condi-
124 tion called *independence* is required. For most practical purposes, to say that two quantities are
125 “independent” is to say that their random components are completely unrelated. To be more
126 rigorous, X and Y are independent if and only if $\Pr[X \in I \text{ and } Y \in J] = \Pr[X \in I] \cdot \Pr[Y \in J]$ for
127 any intervals I and J in the real line, where the symbol \in denotes set membership.

128 When the value of a random variable X is used to estimate the value of an unknown parameter p ,
129 then X is called an *estimator* for p . The *bias* of X is the difference between the mean μ_X and the
130 actual value p . If the bias is zero, then X is said to be *unbiased*; otherwise, X is *biased*.

131 19.2.2 Summary of Terms

132 **arithmetic mean:** The term “arithmetic mean” denotes the estimate of the expectation of a distri-
133 bution calculated by dividing the sum of a set of observed values by the number of values. It is
134 also called the “average.”

- 135 **bias:** If X is an estimator for a parameter p , then the *bias* of X is $\mu_X - p$.
- 136 **coefficient of variation:** The *coefficient of variation* of a nonnegative distribution is the ratio of
137 its standard deviation to its mean.
- 138 **correlated:** Two random variables are *correlated* if their covariance is nonzero.
- 139 **correlation coefficient:** The *correlation coefficient* of two random variables is equal to their
140 covariance divided by the product of their standard deviations.
- 141 **covariance:** The *covariance* of two random variables X and Y , denoted by $\text{Cov}(X, Y)$ or $\sigma_{X, Y}$, is a
142 measure of the association between them, and is defined as $E[(X - \mu_X)(Y - \mu_Y)]$.
- 143 **distribution:** The *distribution* of a random variable is a mathematical description of its possible
144 values and their probabilities. The distribution is uniquely determined by its distribution function.
- 145 **distribution function:** The *distribution function*, or *cumulative distribution function*, of a ran-
146 dom variable X is the function F defined by $F(x) = \text{Pr}[X \leq x]$.
- 147 **estimator:** A random variable whose value is used to estimate an unknown parameter p is called
148 an *estimator* for p .
- 149 **expectation:** The *expectation* of a random variable X , denoted by $E(X)$ or μ_X , is a measure of the
150 center of its distribution and is defined as a probability-weighted average of the possible numer-
151 ical values.
- 152 **expected value:** See *expectation*.
- 153 **independent:** A collection of random variables X_1, X_2, \dots, X_n is *independent* if $\text{Pr}[X_1 \in I_1, X_2 \in I_2,$
154 $\dots, X_n \in I_n] = \text{Pr}[X_1 \in I_1] \cdot \text{Pr}[X_2 \in I_2] \cdots \text{Pr}[X_n \in I_n]$ for all intervals I_1, I_2, \dots, I_n in the real line.
- 155 **mean:** See *expectation*.
- 156 **median:** A *median* of a distribution is any number that splits the range of possible values into
157 two equally likely portions, or, to be more rigorous, a 0.5-quantile.
- 158 **mode:** The *mode* of a distribution is its most probable value.

159 **percentile:** A $100p^{\text{th}}$ percentile of X is the same as a p -quantile of X .

160 **probability density function (pdf):** A *probability density function* for a random variable X is a
161 function $f(x)$ such that the probability of any event $a \leq X \leq b$ is equal to the value of the integral
162 $\int_a^b f(x) dx$. The pdf, when it exists, equals the derivative of the distribution function.

163 **quantile:** A p -quantile of a random variable X is any value x_p such that the probability that $X < x_p$
164 is at most p and the probability that $X \leq x_p$ is at least p .

165 **random variable:** A *random variable* is the numerical outcome of an experiment which pro-
166 duces varying results when repeated.

167 **relative standard deviation (RSD):** See *coefficient of variation*.

168 **relative variance:** The *relative variance* of a random variable is the square of the coefficient of
169 variation.

170 **standard deviation:** The *standard deviation* of a random variable X , denoted by σ_X , is a measure
171 of the width of its distribution, and is defined as the square root of the variance of X .

172 **variance:** The *variance* of a random variable X , denoted by σ_X^2 , $\text{Var}(X)$, or $V(X)$, is defined as
173 $E[(X - \mu_X)^2]$.

174 19.3 Measurement Uncertainty

175 The methods, terms, and symbols recommended by MARLAP for evaluating and expressing
176 measurement uncertainty are described in the *Guide to the Expression of Uncertainty in Meas-*
177 *urement*, hereafter abbreviated as *GUM*, which was published by the International Organization
178 for Standardization (ISO) in 1993 and corrected and reprinted in 1995 (ISO 1995). The methods
179 presented in the *GUM* are summarized in this chapter and adapted for application to radiochem-
180 istry.

181 19.3.1 Measurement, Error, and Uncertainty

182 The result of a measurement is generally used to estimate some physical quantity called the
183 *measurand*. For example, the measurand for a radioactivity measurement might be the activity
184 concentration of ^{238}Pu in a laboratory sample. The measured result may vary with each repetition

185 of the measurement and should therefore be considered a random variable. The difference
186 between the measured result and the actual value of the measurand is the *error* of the measure-
187 ment, which is also a random variable.

188 Measurement error may be caused by *random effects* or *systematic effects* in the measurement
189 process. Random effects cause the measured result to vary randomly when the measurement is
190 repeated. Systematic effects cause the result to tend to differ from the value of the measurand by
191 a constant absolute or relative amount, or to vary in a nonrandom manner. Generally, both
192 random and systematic effects are present in a measurement process.

193 A measurement error produced by a random effect is a *random error*, and an error produced by a
194 systematic effect is a *systematic error*. The distinction between random and systematic errors
195 depends on the specification of the measurement process, since a random error in one measure-
196 ment process may appear systematic in another. For example, a random error in the measurement
197 of the concentration of a radioactive standard solution may be systematic from the point of view
198 of a laboratory that purchases the solution and uses it to calibrate instruments.

199 Measurement errors may also be *spurious errors*, such as those caused by human *blunders* and
200 instrument malfunctions. Blunders and other spurious errors are not taken into account in the
201 statistical evaluation of measurement uncertainty. They should be avoided, if possible, by the use
202 of good laboratory practices, or at least detected and corrected by appropriate quality assurance
203 and quality control activities.

204 The error of a measurement is primarily a theoretical concept, because its value is unknowable.
205 The *uncertainty* of a measurement, however, is a concept with practical uses. According to the
206 *GUM*, the term “uncertainty of measurement” denotes a “parameter, associated with the result of
207 a measurement, that characterizes the dispersion of the values that could reasonably be attributed
208 to the measurand.” The uncertainty of a measured value thus gives a bound for the likely size of
209 the measurement error. In practice, there is seldom a need to refer to the error of a measurement,
210 but an estimate of the uncertainty is required for every measured result.

211 **19.3.2 The Measurement Process**

212 The first step in defining a measurement process is to define the measurand clearly. The specifi-
213 cation of the measurand is always ambiguous to some extent, but it should be as clear as neces-

214 sary for the intended purpose of the data.¹ For example, when measuring the concentration of a
 215 radionuclide in a laboratory sample, it is generally necessary to specify the concentration as of a
 216 certain date and time and whether the entire sample or only a certain fraction is of interest. For
 217 very accurate work, it may be necessary to specify other conditions, such as temperature (e.g.,
 218 concentration per unit volume of liquid at 20°C).

219 Often the measurand is not measured directly but instead an estimate is calculated from the meas-
 220 ured values of other *input quantities*, which have a known mathematical relationship to the
 221 measurand. For example, input quantities in a measurement of radioactivity may include the
 222 gross count, instrument background count, counting efficiency, and test portion size. The second
 223 step in defining the measurement process is therefore to determine the mathematical model for
 224 the relationship between the measurand Y and measurable input quantities X_i on which its value
 225 depends. The relationship may be a simple functional relationship, expressible as $Y =$
 226 $f(X_1, X_2, \dots, X_N)$, or it may happen that Y is most conveniently expressed as the simultaneous
 227 solution of a set of equations.

228 The mathematical model for a radioactivity measurement often has the general form

$$229 \quad Y = \frac{(\text{Gross Instrument Signal}) - (\text{Blank Signal} + \text{Estimated Interferences})}{\text{Sensitivity}}$$

230 Each of the quantities shown here may actually be a more complicated expression. For example,
 231 the sensitivity (the ratio of the net signal to the concentration) may be the product of factors such
 232 as the mass of the test portion, the chemical yield, and the instrument counting efficiency.

233 When the measurement is performed, a value x_i is estimated for each input quantity, X_i , and an
 234 estimated value y of the measurand is calculated using the relationship $y = f(x_1, x_2, \dots, x_N)$.² Since
 235 there is an uncertainty in each *input estimate*, x_i , there is also an uncertainty in the *output*
 236 *estimate*, y . In order to obtain a complete estimate of the uncertainty of y , all input quantities that
 237 could have a potentially significant effect on y should be included in the model.

¹ Because of the unavoidable ambiguity in the specification of the measurand, one should, to be precise, speak of “a value” of the measurand and not “the value.”

² In accordance with the *GUM*, an uppercase Roman letter is used here to denote both the input or output quantity and the random variable associated with its measurement, while a lowercase letter is used for the estimated value of the quantity. For simplicity, in most of the later examples this convention will be abandoned. Only one symbol will be used for the quantity, the random variable, and the estimated value of the quantity.

238 **19.3.3 Analysis of Measurement Uncertainty**

239 Determining the uncertainty of the output estimate y requires that the uncertainties of all the input
240 estimates x_i be determined and expressed in comparable forms. The uncertainty of x_i is expressed
241 in the form of a standard deviation, called the *standard uncertainty* and denoted by $u(x_i)$, or in the
242 form of a variance, denoted by $u^2(x_i)$, which is the square of the standard uncertainty. A standard
243 uncertainty is sometimes informally called a “one-sigma” uncertainty. The ratio $u(x_i) / x_i$ is called
244 the *relative standard uncertainty* of x_i . If the input estimates are potentially correlated, covariance
245 estimates $u(x_i, x_j)$ must also be determined. The covariance $u(x_i, x_j)$ is often recorded and presented
246 in the form of an estimated correlation coefficient, $r(x_i, x_j)$, which is defined as the quotient
247 $u(x_i, x_j) / u(x_i)u(x_j)$. The standard uncertainties and estimated covariances are combined to obtain
248 the *combined standard uncertainty* of y , denoted by $u_c(y)$. (The term “total propagated uncertain-
249 ty,” or TPU, has been used for the same concept; however, MARLAP recommends the ISO
250 terminology.) The square of the combined standard uncertainty, denoted by $u_c^2(y)$, is called the
251 *combined variance*.

252 The process of combining the standard uncertainties of the input estimates x_i to obtain the com-
253 bined standard uncertainty of the output estimate y is called “uncertainty propagation.” Mathe-
254 matical methods for propagating uncertainty and for evaluating the standard uncertainties of the
255 input estimates are described in Section 19.5.

256 Methods for evaluating the standard uncertainties $u(x_i)$ are classified as either Type A or Type B.
257 A *Type A* evaluation of a standard uncertainty $u(x_i)$ may be performed by making a series of inde-
258 pendent measurements of the quantity x_i and calculating the arithmetic mean and experimental
259 standard deviation of the mean. The arithmetic mean is used as the input estimate x_i and the
260 experimental standard deviation of the mean is used as the standard uncertainty $u(x_i)$. There are
261 other Type A methods, but all are based on repeated measurements. Any evaluation of standard
262 uncertainty that is not a Type A evaluation is a *Type B* evaluation.

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

267 A standard uncertainty $u(x_i)$ may be called a “Type A” or “Type B” standard uncertainty, depend-
268 ing on its method of evaluation, but no distinction is made between the two types for the
269 purposes of uncertainty propagation.

270 19.3.4 Corrections for Systematic Effects

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

275 Whenever a previously unrecognized systematic effect is detected, the effect should be investi-
276 gated and either eliminated procedurally or corrected mathematically.

277 19.3.5 Counting Uncertainty

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

283 In many cases the counting uncertainty in a single gross radiation counting measurement can be
284 estimated by the square root of the observed counts. The Poisson counting model, which is the
285 mathematical basis for this rule, is discussed in Section 19.6. Note that the use of this approxi-
286 mation is a Type B evaluation of uncertainty.

287 Historically many radiochemistry laboratories reported only the counting uncertainties of their
288 measured results. MARLAP recommends that a laboratory consider all possible sources of meas-
289 urement uncertainty and evaluate and propagate the uncertainties for all sources believed to be
290 potentially significant in the final result.

291 19.3.6 Expanded Uncertainty

292 The laboratory may report the combined standard uncertainty, $u_c(y)$, or it may multiply $u_c(y)$ by a
293 factor k , called a *coverage factor*, to produce an *expanded uncertainty*, denoted by U , such that
294 the interval from $y - U$ to $y + U$ has a specified high probability p of containing the value of the
295 measurand. The specified probability, p , is called the *level of confidence* or the *coverage proba-*
296 *bility* and is generally only an approximation of the true probability of coverage.

297 When the distribution of the measured result is approximately normal, the coverage factor is
298 often chosen to be $k = 2$ for a coverage probability of approximately 95%. An expanded uncer-

299 tainty calculated with $k = 2$ or 3 is sometimes informally called a “two-sigma” or “three-sigma”
 300 uncertainty. In general, if the desired coverage probability is γ and the combined standard uncer-
 301 tainty is determined accurately, the coverage factor for a normally distributed result is $k = z_{(1+\gamma)/2}$,
 302 which can be found in a table of quantiles of the standard normal distribution (see Table G.1 in
 303 Appendix G).

304 The *GUM* recommends the use of coverage factors in the range 2–3 when the combined standard
 305 uncertainty is determined accurately. Attachment 19C describes a more general procedure for
 306 calculating the coverage factor k_p that gives a desired coverage probability p when there is sub-
 307 stantial uncertainty in the estimate of $u_c(y)$.

308 **19.3.7 Significant Figures**

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

316 **EXAMPLES**

317 318 319	MEASURED VALUE (y)	EXPANDED UNCERTAINTY $U = k u_c(y)$	REPORTED RESULT
320	0.8961	0.0234	0.896 ± 0.023
321	0.8961	0.2342	0.90 ± 0.23
322	0.8961	2.3419	0.9 ± 2.3
323	0.8961	23.4194	1 ± 23
324	0.8961	234.1944	0 ± 230

325 Only final results should be rounded in this manner. Intermediate results in a series of calculation
 326 steps should be carried through all steps with additional figures to prevent unnecessary roundoff
 327 errors. Additional figures are also recommended when the data are stored electronically. Round-
 328 ing should be performed only when the result is reported. (See Section 19.6.10 for a discussion of
 329 the measurement uncertainty associated with rounding.)

330 19.3.8 Reporting the Measurement Uncertainty

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

333 The measured value y and its expanded uncertainty U may be reported in the format $y \pm U$ or
334 $y \pm U$.

335 The plus-minus format may be used to report an expanded uncertainty, but it generally should be
336 avoided when reporting a standard uncertainty, because readers are likely to interpret it as a con-
337 fidence interval. A commonly used shorthand format for reporting a result with its standard
338 uncertainty places the one or two digits of the standard uncertainty in parentheses immediately
339 after the corresponding final digits of the rounded result. For example, if the rounded result of the
340 measurement is 1.92 and the standard uncertainty is 0.14, the result and uncertainty may be
341 shown together as 1.92(14). One may also report the standard uncertainty explicitly.

342 Since laboratories may calculate uncertainties using different methods and report them using
343 different coverage factors, it is a bad practice to report an uncertainty without explaining what it
344 represents. Any analytical report, even one consisting of only a table of results, should state
345 whether the uncertainty is the combined standard uncertainty or an expanded uncertainty, and in
346 the latter case it should also state the coverage factor used and the approximate coverage prob-
347 ability. A complete report should also describe the methods used to calculate the uncertainties.

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

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

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

367 19.3.9 Recommendations

368 MARLAP makes the following recommendations.

- 369 • All radioanalytical laboratories should adopt the terminology and methods of the *Guide*
370 *to the Expression of Uncertainty in Measurement* (ISO 1995) for evaluating and
371 reporting measurement uncertainty.
- 372 • Each measured value should be reported with either its combined standard uncertainty
373 or its expanded uncertainty.
- 374 • The reported measurement uncertainties should be clearly explained. In particular, the
375 coverage factor and approximate coverage probability should be stated whenever an
376 expanded uncertainty is reported.
- 377 • A laboratory should consider all possible sources of measurement uncertainty and
378 evaluate and propagate the uncertainties for all sources believed to be potentially
379 significant in the final result.
- 380 • Each uncertainty should be rounded to two significant figures, and the measured value
381 should be rounded to the same number of decimal places as its uncertainty.
- 382 • All results, whether positive, negative, or zero, should be reported as obtained, together
383 with their uncertainties.

384 19.3.10 Summary of Terms

385 **blunder:** mistake made by a person performing a measurement.

386 **combined standard uncertainty:** standard uncertainty of an output estimate calculated by
387 combining the standard uncertainties of the input estimates. The combined standard uncertainty
388 of y is denoted by $u_c(y)$.

389 **combined variance:** the square of the combined standard uncertainty. The combined variance of
390 y is denoted by $u_c^2(y)$.

391 **counting error:** See *counting uncertainty*. MARLAP uses the term “counting uncertainty” to
392 maintain a clear distinction between the concepts of measurement error and uncertainty.

393 **counting uncertainty:** component of measurement uncertainty caused by the random nature of
394 radioactive decay and radiation counting.

395 **coverage factor:** value k multiplied by the combined standard uncertainty $u_c(y)$ to give the
396 expanded uncertainty U .

397 **coverage probability:** approximate probability that the reported interval will contain the value of
398 the measurand.

399 **error (of measurement):** difference between a measured result and the value of the measurand
400 (cf. uncertainty of measurement).

401 **expanded uncertainty:** product U of the combined standard uncertainty of a measured value y
402 and a coverage factor k chosen so that the interval from $y - U$ to $y + U$ has a desired high proba-
403 bility of containing the value of the measurand Y .

404 **GUM:** abbreviation used in this chapter for the *Guide to the Expression of Uncertainty in*
405 *Measurement* (ISO 1995).

406 **input estimate:** measured value of an input quantity.

407 **input quantity:** any of the quantities in a mathematical measurement model whose values are
408 measured and used to calculate the value of another quantity, called the *output quantity*.

409 **level of confidence:** See *coverage probability*.

410 **measurand:** quantity subject to measurement.

411 **output estimate:** calculated value of an output quantity.

412 **output quantity:** the quantity in a mathematical measurement model whose value is calculated
413 from the measured values of other quantities in the model.

414 **random effect:** any effect in a measurement process which causes the measured result to vary
415 randomly when the measurement is repeated.

416 **random error:** a measurement error which varies randomly when the measurement is repeated
417 — caused by random effects.

418 **relative standard uncertainty:** the ratio of the standard uncertainty of a measured result to the
419 result itself. The relative standard uncertainty of x may be denoted by $u_r(x)$.

420 **sigma (σ):** The term “sigma” is sometimes used *informally* to mean “standard uncertainty,” and
421 “ k -sigma” is used to mean an expanded uncertainty calculated using the coverage factor k . The
422 symbol σ and the term “sigma” are more properly used to denote a true standard deviation.

423 **spurious error:** a measurement error caused by a human blunder, instrument malfunction, or
424 other unexpected or abnormal event

425 **standard uncertainty:** uncertainty of a measured value expressed as a standard deviation —
426 often called a “1-sigma” uncertainty. The standard uncertainty of x is denoted by $u(x)$.

427 **systematic effect:** any effect in a measurement process which does not vary randomly when the
428 measurement is repeated.

429 **systematic error:** a measurement error which does not vary randomly when the measurement is
430 repeated — caused by systematic effects.

431 **total propagated uncertainty (TPU):** See *combined standard uncertainty*, which is the
432 preferred term.

433 **Type A evaluation:** experimental evaluation of a standard uncertainty or covariance using
434 repeated measurements.

435 **Type B evaluation:** evaluation of a standard uncertainty or covariance by a method that is not a
436 Type A method.

437 **uncertainty (of measurement):** “parameter, associated with the result of a measurement, that
438 characterizes the dispersion of the values that could reasonably be attributed to the measurand”
439 (ISO 1993a).

440 **uncertainty propagation:** mathematical technique for combining the standard uncertainties of
441 the input estimates for a mathematical model to obtain the combined standard uncertainty of the
442 output estimate.

443 **19.4 Detection and Quantification Capability**

444 **19.4.1 Analyte Detection Decisions**

445 An obvious question to be answered following the analysis of a laboratory sample is: “Does the
446 sample contain a positive amount of the analyte?” Uncertainty in the measured value often makes
447 the question difficult to answer. There are different methods for making a *detection decision*, but
448 the methods most often used in radiochemistry involve the principles of statistical hypothesis
449 testing.

450 Hypothesis testing has been used for analyte detection in radiochemistry since at least 1962. Two
451 influential early publications on the subject were Altshuler and Pasternack 1963 and Currie 1968.
452 Other important but perhaps less well-known documents were Nicholson 1963 and 1966. Most
453 approaches to the detection problem have been similar in principle, but there has been inadequate
454 standardization of terminology and methodology. However, there has been recent progress. In
455 1995 the International Union of Pure and Applied Chemistry (IUPAC) published “Nomenclature
456 in Evaluation of Analytical Methods Including Detection and Quantification Capabilities”
457 (IUPAC 1995), which recommends a uniform approach to defining various performance char-
458 acteristics of any chemical measurement process, including detection and quantification limits;
459 and in 1997 the International Organization for Standardization (ISO) issued the first part of ISO
460 11843 “Capability of Detection,” a two-part standard which deals with issues of detection in an
461 even more general context of measurement (ISO 1997). Part 1 of ISO 11843 includes terms and
462 definitions. Part 2, which is not available at the time of this writing, will deal with methodology.
463 Although members of the IUPAC and ISO working groups collaborated during the development
464 of their guidelines, substantial differences between the final documents remain. MARLAP
465 follows both the ISO and IUPAC guidelines where they agree but prefers the definitions of ISO
466 11843-1 for the critical value and minimum detectable value, relating them to the terminology
467 and methodology already familiar to most radiochemists.

468 In July 2000, ISO also published the first three parts of ISO 11929 “Determination of the Detec-
469 tion Limit and Decision Threshold for Ionizing Radiation Measurements” (ISO 2000a–c). Unfor-
470 tunately, ISO 11929 is not completely consistent with either the earlier ISO standard or the
471 IUPAC recommendations.

472 In the terminology of ISO 11843-1, the analyte concentration of a laboratory sample is the *state*
473 *variable*, denoted by Z , which represents the state of the material being analyzed. Blank material
474 is said to be in the *basic state*. The state variable cannot be observed directly, but it is related to
475 an observable *response variable*, denoted by Y , through a *calibration function* F , the mathemat-
476 ical relationship being written as $Y = F(Z)$. In radiochemistry the response variable Y is most
477 often an instrument signal, such as the number of counts observed. The difference between the
478 state variable Z and its value in the basic state is called the *net state variable*, which is denoted
479 by X . In radiochemistry there generally is no difference between the state variable and the net
480 state variable, because the basic state is represented by material whose analyte concentration is
481 zero. (In principle the basic state might correspond to a positive concentration, but MARLAP
482 does not address this scenario.)

483 A detection decision requires a choice between two hypotheses about the material being ana-
484 lyzed. The first hypothesis is the “null hypothesis” H_0 : The analyte concentration of the material
485 is no greater than that of the blank (i.e., the material is in the basic state). The second hypothesis
486 is the “alternative hypothesis” H_1 : The analyte concentration of the material is greater than that of
487 the blank. The choice between the two hypotheses is based on the observed value of the response
488 variable Y . The value of Y must exceed a certain threshold value to justify rejection of the null
489 hypothesis. This threshold is called the *critical value* of the response variable and is denoted
490 by y_c . The calculation of y_c requires the choice of a *significance level* for the test. The signifi-
491 cance level is the probability α that the null hypothesis will be rejected in a situation where it is
492 in fact true (i.e., a “type I error,” or “false positive”). The significance level α is usually chosen to
493 be 0.05. This means that when a blank sample is analyzed, there is a 5% probability of incor-
494 rectly deciding that the analyte is present. A smaller value of α makes type I errors less likely, but
495 also makes type II errors (“false negatives”) more likely when the laboratory sample concentra-
496 tion is near the blank concentration.

497 The term “blank” here may mean any of several types of blanks, including instrument blanks (or
498 backgrounds) and reagent blanks. The blank is chosen to provide an estimate of the mean signal
499 produced by an actual sample that contains none of the analyte, whether the signal is produced by
500 the instrument background, contaminated reagents, or other causes.

501 The inverse F^{-1} of the calibration function is sometimes called the *evaluation function* (IUPAC
502 1995). The evaluation function, which gives the value of the net concentration in terms of the
503 response variable, is closely related to the *mathematical model* described in Section 19.3.2.

504 The *critical value of the analyte concentration* x_C , according to the ISO definition, is the value
505 obtained by applying the evaluation function F^{-1} to the critical value of the response variable y_C .
506 Thus, $x_C = F^{-1}(y_C)$. In radiochemistry this formula typically involves division by the counting
507 efficiency, test portion size, chemical yield, decay factor, and possibly other factors. In ANSI
508 N42.23, the same value x_C is called the *decision level concentration*, or DLC (ANSI 1996b).

509 According to ISO 11843-1, a detection decision involves the critical value of the response
510 variable, or gross instrument signal, which, in a radioactivity measurement, is typically a total
511 count or count rate. However, it has become standard practice in radioanalysis to use instead the
512 critical value of the *net* instrument signal, which is calculated from the gross signal by subtract-
513 ing the estimated blank value and any interferences. This practice is consistent with the recom-
514 mendations of IUPAC (1995), where the critical value of the net instrument signal S is denoted
515 by S_C . In principle, either approach should lead to the same detection decision.

516 Since the term “critical value” alone is ambiguous, one should specify the variable to which the
517 term refers. For example, one may discuss the critical (value of the) analyte concentration, the
518 critical (value of the) net count, or the critical (value of the) gross count.

519 Section 19.7.1 and Section 19D.2 of Attachment 19D provide more information on the calcula-
520 tion of critical values.

521 **19.4.2 The Minimum Detectable Concentration**

522 The *minimum detectable concentration* is the concentration of analyte that must be present in a
523 laboratory sample to give a specified probability $1 - \beta$ of detection. Then β is the probability of
524 failing to reject the null hypothesis when it is false (i.e., a “type II error,” or “false negative”).
525 The minimum detectable concentration is often abbreviated as MDC. In the ISO terminology the
526 MDC is called the *minimum detectable value of the net state variable*, denoted by x_D , which is
527 defined as the smallest (true) value of the net state variable that gives a specified high probability
528 $1 - \beta$ that the value of the response variable will exceed its critical value, thus leading one to
529 conclude correctly that the material analyzed is not in the basic state (i.e., the material is not
530 blank). The relationship between the critical value and the minimum detectable value of the net
531 state variable is shown in Figure 19.3.

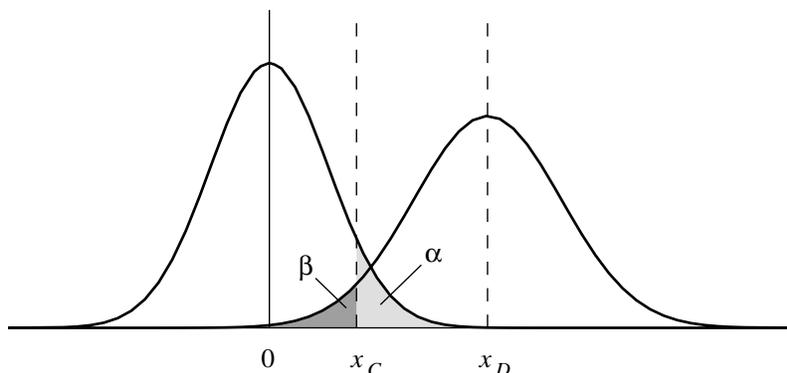


FIGURE 19.3 — The critical value x_C and minimum detectable value x_D of the net state variable

532 Sections 19.7.2 and 19D.3 provide more information about the calculation of the minimum
 533 detectable concentration.

534 When the quantity being measured is the total amount of analyte in an item and not an analyte
 535 concentration, the minimum detectable value is sometimes called the *minimum detectable*
 536 *amount*, which may be abbreviated as MDA. This chapter focuses on the MDC, but with few
 537 changes the guidance is also applicable to the MDA.

538 While project planners and laboratories have some flexibility in choosing the significance level α
 539 used for detection decisions, the MDC is usually calculated with $\alpha = \beta = 0.05$. The use of stan-
 540 dard values for α and β allows meaningful comparison of analytical procedures.

541 The MDC concept has generated controversy among radiochemists for years and has frequently
 542 been misinterpreted and misapplied. The term must be carefully and precisely defined to prevent
 543 confusion. The MDC is by definition the *true* concentration of analyte required to give a speci-
 544 fied high probability that the *measured* response will be greater than the critical value. Thus, the
 545 common practice of comparing a measured concentration to the MDC to make a detection
 546 decision is not defensible.

547 There are still disagreements about the proper uses of the MDC concept. Some define the MDC
 548 strictly as an estimate of the nominal detection capability of a *measurement process*. Those in
 549 this camp consider it invalid to compute an MDC for each *measurement* using sample-specific
 550 information such as test portion size, chemical yield, and decay factors (e.g., ANSI N42.23). The
 551 opposing view is that the “sample-specific” MDC is a useful measure of the detection capability

552 of the measurement process, not just in theory, but as it actually performed. The sample-specific
553 MDC may be used, for example, to determine whether an analysis that has failed to detect the
554 analyte of interest should be repeated because it did not have the required or promised detection
555 capability.

556 Neither version of the MDC can legitimately be used as a threshold value for a detection deci-
557 sion. The definition of the MDC presupposes that an appropriate detection threshold (i.e., the
558 critical value) has already been defined.

559 Many experts strongly discourage the reporting of a sample-specific MDC because of its limited
560 usefulness and the likelihood of its misuse. Nevertheless, this practice has become firmly estab-
561 lished at many laboratories and is expected by many users of radioanalytical data. Furthermore,
562 NUREG/CR-4007 states plainly that “the critical (decision) level and detection limit [MDC]
563 really do vary with the nature of the sample” and that “proper assessment of these quantities
564 demands relevant information on each sample, unless the variations among samples (e.g., inter-
565 ference levels) are quite trivial” (NRC 1984).

566 Since a sample-specific MDC is calculated from measured values of input quantities such as the
567 chemical yield, counting efficiency, test portion size, and background level, the MDC estimate
568 has a combined standard uncertainty, which in principle can be obtained by uncertainty propa-
569 gation.

570 In the calculation of a sample-specific MDC, the treatment of any *randomly varying but precisely*
571 *measured* quantities, such as the chemical yield, is important and may not be identical at all lab-
572 oratories. The most common approach to this calculation uses the measured value and ignores
573 the variability of the quantity. For example, if the chemical yield routinely varies between 0.85
574 and 0.95, but for a particular analysis the yield happens to be 0.928, the MDC for that analysis
575 would be calculated using the value 0.928 with no consideration of the typical range of yields. A
576 consequence of this approach is that the MDC varies randomly when the measurement is
577 repeated under similar conditions; or, in other words, the sample-specific MDC with this
578 approach is a random variable. The nominal MDC for the measurement process is a constant —
579 *not* a random variable.

580 If sample-specific MDCs are reported, it must be clear that no measured value should ever be
581 compared to an MDC to make a detection decision. In certain cases it may be valid to compare
582 the sample-specific MDC to a required detection limit to determine whether the laboratory has
583 met contractual or regulatory requirements (remembering to consider the uncertainty of the MDC
584 estimate), and in general it may be informative to both laboratory personnel and data users to

585 compare sample-specific MDCs to nominal estimates, but other valid uses for the sample-
586 specific MDC are rare.

587 **19.4.3 Differences between the ISO and IUPAC Definitions**

588 The ISO and IUPAC guidance documents give different definitions for some of the terms listed
589 above and promote somewhat different concepts. In general, the IUPAC approach is to define the
590 “critical value” and “minimum detectable value” separately for the signal and concentration
591 domains. A detection decision may be made in either domain, but the outcome of the decision
592 may depend on which domain is chosen. With the ISO approach the outcome does not depend on
593 the domain. Either domain may be chosen, but *in effect* all detection decisions are made in the
594 signal domain.

595 The IUPAC and ISO approaches to detection in the signal domain, although expressed differ-
596 ently, are effectively equivalent. (IUPAC bases detection decisions on the net signal S , whereas
597 ISO bases detection decisions on the gross signal Y .) The more important differences are in the
598 concentration domain (X). For example, according to IUPAC, the critical analyte concentration
599 x_C is determined from the distribution of the measured concentration X , taking into account its
600 overall measurement uncertainty. According to ISO, x_C is simply a function of y_C , the critical
601 value of the response variable. Since x_C is related to y_C in the same way that X is related to Y , it
602 makes no difference whether detection decisions are based on X or Y — the outcome is the same.

603 The IUPAC guidance defines the minimum detectable concentration x_D as the smallest concentra-
604 tion that gives a specified high probability of obtaining a measured concentration greater than x_C ,
605 which is inconsistent with the ISO guidance because of the differing definitions of x_C .

606 One consequence of the IUPAC definitions is that the measurement variances of sensitivity fac-
607 tors such as the test portion size, counting efficiency, and chemical yield increase the values of x_C
608 and x_D because they increase the variance of X . According to the ISO definitions, these variances
609 do not increase the values of x_C and x_D , although they generate uncertainties in the estimates of x_C
610 and x_D . In principle, the ISO definitions imply that variability in the true values of these sensitiv-
611 ity factors *does* increase x_D , although the draft implementation guidance in ISO 11843-2 appar-
612 ently does not deal with the issue.

613 As stated above, MARLAP adopts the ISO definitions but also follows the IUPAC guidance
614 where it does not contradict the definitions of ISO 11843-1. The draft implementation guidance
615 in ISO 11843-2 appears not to be designed for typical radioanalytical measurement processes.

616 19.4.4 Other Detection Terminologies

617 Another term frequently used for a measure of detection capability is the “lower limit of detec-
618 tion,” or LLD (Altshuler 1963, EPA 1980, NRC 1984). Unfortunately this term has been used
619 with more than one meaning. In *Upgrading Environmental Radiation Data* (EPA 1980), the LLD
620 is defined as a measure of the detection capability of an instrument and is expressed as an activ-
621 ity. However, the Nuclear Regulatory Commission defines the LLD to be identical to the MDC
622 when $\alpha = \beta = 0.05$ (see, for example, NUREG/CR-4007). It is thus a measure of the detection
623 capability of a measurement process and is expressed as an activity *concentration*.

624 The term “detection limit” is often used as a synonym for “MDC” or for “minimum detectable
625 value” of any other measured quantity.

626 Many other terms have been used to describe detection capabilities of measurement procedures.
627 Most of them will not be listed here, but one term deserves attention because of the possibility of
628 its confusion with the MDC. The *method detection limit*, or MDL, is a measure of detection
629 capability used routinely in the context of analyzing samples for chemical contaminants.

630 The term “method detection limit” is defined in the Code of Federal Regulations. In Title 40
631 CFR Part 136, Appendix B, the following definition appears:

632 The method detection limit (MDL) is defined as the minimum concentration of a
633 substance that can be measured and reported with 99% confidence that the analyte
634 concentration is greater than zero and is determined from analysis of a sample in a
635 given matrix containing the analyte.

636 The definition is later clarified somewhat by a statement that the MDL “is used to judge the sig-
637 nificance of a single measurement of a future sample.” Thus, the MDL serves as a critical value;
638 however, it is also used as a measure of detection capability, like an MDC. Note that, in
639 MARLAP’s usage, the “method detection limit” is not truly a detection limit.

640 The similarity between the abbreviations MDC and MDL tends to produce confusion. The term
641 “method detection limit” is seldom used in the context of radioanalysis except when the analyt-
642 ical method is one that is commonly used to measure stable elements (e.g., ICP/MS methods), or
643 when the term is misused by those who are more familiar with the terminology of hazardous
644 chemical analysis. The confusion is made worse by the fact that “MDL” is sometimes interpreted
645 by radiochemists as an abbreviation for nonstandard terms such as “minimum detectable level”
646 and “minimum detectable limit,” the use of which MARLAP strongly discourages.

647 **19.4.5 The Minimum Quantifiable Concentration**

648 The *minimum quantifiable concentration*, or the *minimum quantifiable value* of the analyte con-
649 centration, is defined as the concentration of analyte in a laboratory sample at which the measure-
650 ment process gives results with a specified relative standard deviation.³ A relative standard devi-
651 ation of 10% is usually specified, although other values are possible (see for example MARLAP
652 Appendix C). Since ISO 11843 addresses detection capability but not quantification capability,
653 MARLAP follows IUPAC guidance in defining “minimum quantifiable value” (IUPAC 1995).
654 IUPAC defines both the minimum quantifiable instrument signal and the minimum quantifiable
655 concentration, although MARLAP considers only the latter. In this document the minimum quan-
656 tifiable concentration will be abbreviated as MQC and denoted in equations by x_Q .

657 The term “quantification limit” may be used as a synonym for “minimum quantifiable concentra-
658 tion” or for “minimum quantifiable value” of any other measured quantity.

659 Section 19.7.3 provides more information about the calculation of the minimum quantifiable
660 concentration.

661 Historically much attention has been given to the detection capabilities of radioanalytical meas-
662 urement processes, but less attention has been given to quantification capabilities, although for
663 some analytical projects, quantification capability may be a more relevant issue. For example,
664 suppose the purpose of a project is to determine whether the ²²⁶Ra concentration in soil from a
665 site is below an action level. Since ²²⁶Ra occurs naturally in almost any type of soil, the analyte
666 may be assumed to be present in every sample, making detection decisions irrelevant. The MDC
667 of the measurement process obviously should be less than the action level, but a more important
668 question is whether the MQC is less than the action level (see also Chapter 3 and Appendix C).

³ The MQC is defined in terms of the relative standard *deviation* of the estimator — not the relative standard *uncertainty* of the measured result. The standard uncertainty is generally an estimate of the standard deviation.

669 **19.4.6 Recommendations**

670 MARLAP makes the following recommendation.

- 671 • A measurement result should not be compared to the minimum detectable concentra-
672 tion to make an analyte detection decision. A detection decision may be made by
673 comparing the gross signal, net signal, or measured analyte concentration to its
674 corresponding critical value.

675 **19.4.7 Summary of Terms**

676 **basic state:** in radiochemistry, the chemical composition of blank material.

677 **critical level:** See *critical value*.

678 **critical value:** in the context of analyte detection, the minimum value of the response variable
679 (or the measured analyte concentration) required to give confidence that a positive amount of
680 analyte is present in the material analyzed.

681 **decision level:** See *critical value*.

682 **detection limit:** See *minimum detectable value*.

683 **false negative:** See *type I decision error*. This chapter avoids the terms “false negative” and
684 “false positive,” because they may be confusing in some contexts.

685 **false positive:** See *type II decision error*.

686 **lower limit of detection (LLD):** (1) “the smallest concentration of radioactive material in a
687 sample that will yield a net count, above the measurement process (MP) blank, that will be
688 detected with at least 95% probability with no greater than a 5% probability of falsely concluding
689 that a blank observation represents a ‘real’ signal” (NRC 1984); (2) “an estimated detection limit
690 that is related to the characteristics of the counting instrument” (EPA 1980).

691 **method detection limit (MDL):** “the minimum concentration of a substance that can be meas-
692 ured and reported with 99% confidence that the analyte concentration is greater than zero ...
693 determined from analysis of a sample in a given matrix containing the analyte” (40 CFR 136,
694 Appendix B).

- 695 **minimum detectable amount (MDA):** the minimum detectable value of the total amount of
696 analyte in the sample being analyzed.
- 697 **minimum detectable concentration (MDC):** the minimum detectable value of the analyte con-
698 centration in a laboratory sample.
- 699 **minimum detectable value:** the smallest value of the net state variable (amount or concentration
700 of analyte) that ensures a specified high probability $1 - \beta$ of detection.
- 701 **minimum quantifiable concentration (MQC):** the minimum quantifiable value of the analyte
702 concentration in a laboratory sample.
- 703 **minimum quantifiable value:** the smallest value of the net state variable (analyte amount or
704 concentration) that ensures the relative standard deviation of the measurement is not greater than
705 a specified value, usually 10%.
- 706 **net state variable (X):** the difference between the state variable Z and its value in the basic state
707—in radiochemistry, usually equal to Z , because the value of Z in the basic state is zero.
- 708 **quantification limit:** See *minimum quantifiable value*.
- 709 **response variable (Y):** the variable that gives the observable result of a measurement—in radio-
710 chemistry, typically a gross count or count rate.
- 711 **significance level (α):** in a hypothesis test, the probability of a type I decision error.
- 712 **state variable (Z):** the quantity that describes the state of the material analyzed—in radiochem-
713 istry, usually the analyte activity concentration.
- 714 **type I decision error:** in a hypothesis test, the error made by rejecting the null hypothesis when
715 it is true (a “false positive”).
- 716 **type II decision error:** in a hypothesis test, the error made by failing to reject the null hypothesis
717 when it is false (a “false negative”).

718 19.5 Procedures for Estimating Uncertainty

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

- 721 1. Identify the measurand Y and all the input quantities X_i for the mathematical model.
722 Include all quantities whose variability or uncertainty could have a potentially significant
723 effect on the result. Express the mathematical relationship $Y = f(X_1, X_2, \dots, X_N)$ between the
724 measurand and the input quantities.
- 725 2. Determine an estimate x_i of the value of each input quantity X_i (an “input estimate,” as
726 defined in Sections 19.3.2 and 19.3.9).
- 727 3. Evaluate the standard uncertainty $u(x_i)$ for each input estimate x_i , using either a Type A or
728 Type B method of evaluation (see Section 19.5.2).
- 729 4. Evaluate the covariances $u(x_i, x_j)$ for all pairs of input estimates with potentially
730 significant correlations.
- 731 5. Calculate the estimate y of the measurand from the relationship $y = f(x_1, x_2, \dots, x_N)$, where f
732 is the function determined in Step 1.
- 733 6. Determine the combined standard uncertainty $u_c(y)$ of the estimate y (see Section 19.5.3).
- 734 7. Multiply $u_c(y)$ by a coverage factor k to obtain the expanded uncertainty U such that the
735 interval $[y - U, y + U]$ can be expected to contain the value of the measurand with a
736 specified probability (see Section 19.3.6 and Attachment 19C).
- 737 8. Report the result as $y \pm U$ with the unit of measure, and, at a minimum, state the coverage
738 factor used to compute U and the estimated coverage probability.

739 19.5.1 Identifying Sources of Uncertainty

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

744 After all conceivable sources of uncertainty are listed, they should be categorized as either poten-
 745 tially significant or negligible. Each uncertainty that is potentially significant should be evaluated
 746 quantitatively. In particular, counting uncertainty, pipetting and weighing uncertainties, and
 747 uncertainties in standard concentrations should always be evaluated. Other possible causes of
 748 uncertainty include source geometry and placement, variable instrument backgrounds and effi-
 749 ciencies, time measurements used in decay and ingrowth calculations, instrument dead-time
 750 corrections, approximation errors in simplified mathematical models, impurities in reagents, and
 751 uncertainties in the published values for half-lives and radiation emission probabilities.

752 19.5.2 Evaluation of Standard Uncertainties

753 Calculating the combined standard uncertainty of an output estimate $y = f(x_1, x_2, \dots, x_N)$ requires
 754 the estimation of the standard uncertainty of each input estimate x_i . As stated earlier, methods for
 755 evaluating standard uncertainties are classified as either “Type A” or “Type B.” A Type A eval-
 756 uation of an uncertainty uses a series of measurements to estimate the standard deviation empiri-
 757 cally. Any other method of evaluating an uncertainty is a Type B method.

758 19.5.2.1 Type A Evaluations

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

$$\bar{X}_i = \frac{1}{n} \sum_{k=1}^n X_{i,k} \quad (19.1)$$

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

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

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

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

765 The experimental standard deviation of the mean is also commonly called the “standard error of
766 the mean.”

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

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

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

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

783 **EXAMPLE:** Ten independent measurements of a quantity X_i are made, yielding the values

784 12.132 12.139 12.128 12.133 12.132
785 12.135 12.130 12.129 12.134 12.136

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

787

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

788 The standard uncertainty of x_i is

$$\begin{aligned}
 u(x_i) = s(\bar{X}_i) &= \sqrt{\frac{1}{n(n-1)} \sum_{k=1}^n (X_{i,k} - \bar{X}_i)^2} \\
 &= \sqrt{\frac{1}{10(10-1)} \sum_{k=1}^{10} (X_{i,k} - 12.1328)^2} \\
 &= \sqrt{1.12888 \times 10^{-6}} = 0.0011
 \end{aligned}$$

790 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 $(X_{i,1}, X_{j,1}), (X_{i,2}, X_{j,2}), \dots, (X_{i,n}, X_{j,n})$, the *experimental covariance* of the values is

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

794 and the *experimental covariance of the means* \bar{X}_i and \bar{X}_j is

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

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

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

796 An evaluation of variances and covariances of parameters determined by the method of least
797 squares may also be a Type A evaluation (see Attachment 19B).

798 19.5.2.2 Type B Evaluations

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

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

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

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

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

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

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

816 **EXAMPLE:** A strontium carrier solution is prepared by dissolving strontium nitrate in acidified
817 water. The purity, P , of the strontium nitrate is stated to be 99.9%, or 0.999, but no tolerance
818 or uncertainty is provided. By default, a rectangular distribution with half-width $1 - P$, or
819 0.001, is assumed. So, the standard uncertainty of P is evaluated as $u(P) = 0.001 / \sqrt{3} =$
820 0.00058.

821 If the value of x is believed to lie between a lower bound a_- and an upper bound a_+ , but values
 822 near these two bounds are considered less likely than those near the midpoint, then a symmetric
 823 *trapezoidal* distribution may be used to obtain the input estimate and its standard uncertainty (see
 824 Section 19A.7 in Attachment 19A). If the ratio of the width of the trapezoid at its top to the width
 825 at its base is β , where $0 < \beta < 1$, then the input estimate is the midpoint $x = (a_- + a_+) / 2$, and its
 826 standard uncertainty is

$$u(x) = \frac{(a_+ - a_-)}{2} \sqrt{\frac{1 + \beta^2}{6}} \quad (19.9)$$

827 As β approaches zero, the trapezoidal distribution becomes *triangular*. As β approaches one, the
 828 trapezoidal distribution becomes rectangular.

829 **EXAMPLE:** Extreme bounds for a quantity X are estimated to be 34.3 and 34.5, with values
 830 between 34.35 and 34.45 considered most likely. Using the trapezoidal distribution with
 831 $a_- = 34.3$, $a_+ = 34.5$, and $\beta = (34.45 - 34.35) / (34.5 - 34.3) = 0.5$, one obtains the input esti-
 832 mate $x = 34.4$ and the standard uncertainty $u(x) = \frac{34.5 - 34.3}{2} \sqrt{\frac{1 + 0.5^2}{6}} = 0.046$.

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

836 **EXAMPLE:** The uncertainty for a measured concentration x is stated to be 0.015 Bq g^{-1} and the
 837 stated multiplier is 2. So, the standard uncertainty of x is $u(x) = 0.015 / 2 = 0.0075 \text{ Bq g}^{-1}$.

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

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

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

844 **EXAMPLE:** The activity concentration x of a commercial standard solution is stated to lie
845 within the interval $4530 \pm 64 \text{ Bq g}^{-1}$ with 95% confidence. The standard uncertainty may
846 therefore be evaluated as $u(x) = 64 / z_{0.975} = 64 / 1.96 = 33 \text{ Bq g}^{-1}$.

847 19.5.3 Combined Standard Uncertainty

848 Consider the mathematical model $Y = f(X_1, X_2, \dots, X_N)$. If x_1, x_2, \dots, x_N are measured values of the
849 input quantities X_i and $y = f(x_1, x_2, \dots, x_N)$ is the calculated value of the measurand Y , the variance
850 of y is estimated using the following formula.

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

The Uncertainty Propagation Formula

851 Here $u^2(x_i)$ denotes the estimated variance of x_i , or the square of its standard uncertainty; $u(x_i, x_j)$
852 denotes the estimated covariance of x_i and x_j ; $\partial y / \partial x_i$ (or $\partial f / \partial x_i$) denotes the partial derivative of
853 Y with respect to X_i evaluated at the measured values x_1, x_2, \dots, x_N ; and $u_c(y)$ denotes the com-
854 bined standard uncertainty of y . The partial derivatives $\partial y / \partial x_i$ are called *sensitivity coefficients*.

855 The preceding formula, called the “law of propagation of uncertainty” in the *GUM*, will be called
856 the “uncertainty propagation formula” in this document.

857 If the input estimates x_1, x_2, \dots, x_N are uncorrelated, the uncertainty propagation formula reduces
858 to

$$u_c^2(y) = \sum_{i=1}^N \left(\frac{\partial y}{\partial x_i} \right)^2 u^2(x_i) \quad (19.12)$$

859 Equation 19.12 is only valid when the input estimates are uncorrelated. Although this case occurs
860 frequently in practice, there are notable exceptions. When input estimates are obtained using the
861 same measuring devices or the same standard solutions, or when they are calculated from the
862 same data, there is a potential for correlation. For example, instrument calibration parameters
863 determined by least-squares analysis may be strongly correlated. Fortunately, the method of least

TABLE 19.1 — Applications of the uncertainty propagation formula

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

864 squares provides covariance estimates with almost no additional effort (see Attachment 19B). In
 865 general, ignoring correlations between the input estimates may lead to overestimation or under-
 866 estimation of the combined standard uncertainty.

867 Table 19.1 shows how to propagate uncertainties in some common cases.

868 The product of $|\partial y / \partial x_i|$ and the standard uncertainty $u(x_i)$ is called the *component* of the
 869 combined standard uncertainty $u_c(y)$ generated by the standard uncertainty of x_i , and may be

870 denoted by $u_i(y)$. When all the input estimates are uncorrelated, the combined standard uncer-
 871 tainty may be written in terms of its components as follows.

$$u_c^2(y) = \sum_{i=1}^N u_i^2(y) \quad (19.13)$$

872 Since $u_c^2(y)$ is the sum of the squares of the components $u_i(y)$, the combined standard uncertainty
 873 tends to be determined primarily by its largest components.

874 EXAMPLE

875 **Problem:** A 6000-s gross alpha measurement is performed on a test source prepared by evap-
 876 orating water on a stainless steel planchet. The measurement produces 120 alpha counts. The
 877 preceding background measurement on the instrument had a duration of 6000 s and produced
 878 42 alpha counts. The estimated alpha counting efficiency is 0.223 with a standard uncertainty
 879 of 0.015. The sample volume analyzed is 0.05000 L, with a standard uncertainty of 0.00019 L.
 880 The alpha emission rate per unit volume is described by the mathematical model

$$881 \quad A = \frac{N_S / t_S - N_B / t_B}{\epsilon V}$$

882 where

883 N_S is the source count ($N_S = 120$)
 884 N_B is the background count ($N_B = 42$)
 885 t_S is the source count time ($t_S = 6000$)
 886 t_B is the background count time ($t_B = 6000$)
 887 ϵ is the counting efficiency ($\epsilon = 0.223$)
 888 V is the volume analyzed ($V = 0.05000$)

889 What is the output estimate A and what is its combined standard uncertainty, $u_c(A)$?

890 **Solution:** First compute the output estimate A (alphas per second per liter).

$$891 \quad A = \frac{N_S / t_S - N_B / t_B}{\epsilon V} = \frac{120/6000 - 42/6000}{(0.223)(0.05000)} \approx 1.17$$

892 Then compute the combined standard uncertainty $u_c(A)$. The only uncertainties included in the
 893 model will be those associated with the counts N_S and N_B , the efficiency ϵ , and the volume V .
 894 There is no reason to suspect correlations between the measured values; so, the uncertainty
 895 propagation formula becomes

$$896 \quad u_c^2(A) = \left(\frac{\partial A}{\partial N_S} \right)^2 u^2(N_S) + \left(\frac{\partial A}{\partial N_B} \right)^2 u^2(N_B) + \left(\frac{\partial A}{\partial \epsilon} \right)^2 u^2(\epsilon) + \left(\frac{\partial A}{\partial V} \right)^2 u^2(V)$$

897 The partial derivatives are evaluated as follows:

$$898 \quad \begin{aligned} \frac{\partial A}{\partial N_S} &= \frac{1}{t_S \epsilon V} & \frac{\partial A}{\partial N_B} &= \frac{-1}{t_B \epsilon V} & \frac{\partial A}{\partial \epsilon} &= -\frac{N_S/t_S - N_B/t_B}{\epsilon^2 V} & \frac{\partial A}{\partial V} &= -\frac{N_S/t_S - N_B/t_B}{\epsilon V^2} \\ &= 0.0149477 & &= -0.0149477 & &= -5.22834 & &= -23.3184 \end{aligned}$$

899 The Poisson model is used for the standard uncertainties of the counts N_S and N_B . So,

$$900 \quad u^2(N_S) = N_S = 120 \quad \text{and} \quad u^2(N_B) = N_B = 42$$

901 Recall from the statement of the problem that $u(\epsilon) = 0.015$ and $u(V) = 0.00019$. When the
 902 values of all these expressions are substituted into the uncertainty propagation formula, the
 903 combined variance is $u_c^2(A) = 0.0424$; so, the combined standard uncertainty is $u_c(A) =$
 904 $\sqrt{0.0424} \approx 0.21$.

905 It is helpful to remember certain special forms of the uncertainty propagation formula. For
 906 example, if the values x_1, x_2, \dots, x_n and z_1, z_2, \dots, z_m are uncorrelated and nonzero, the combined
 907 standard uncertainty of $y = \frac{x_1 x_2 \dots x_n}{z_1 z_2 \dots z_m}$ may be calculated from the formula

$$u_c^2(y) = y^2 \left(\frac{u^2(x_1)}{x_1^2} + \frac{u^2(x_2)}{x_2^2} + \dots + \frac{u^2(x_n)}{x_n^2} + \frac{u^2(z_1)}{z_1^2} + \frac{u^2(z_2)}{z_2^2} + \dots + \frac{u^2(z_m)}{z_m^2} \right) \quad (19.14)$$

908 As another example, suppose $y = \frac{f(x_1, x_2, \dots, x_n)}{z_1 z_2 \dots z_m}$, where f is some specified function of x_1, x_2, \dots, x_n ,
 909 all the z_i are nonzero, and all the input estimates are uncorrelated. Then

$$u_c^2(y) = \frac{u_c^2(f(x_1, x_2, \dots, x_n))}{z_1^2 z_2^2 \dots z_m^2} + y^2 \left(\frac{u^2(z_1)}{z_1^2} + \frac{u^2(z_2)}{z_2^2} + \dots + \frac{u^2(z_m)}{z_m^2} \right) \quad (19.15)$$

910 Equation 19.15 is particularly useful in radioanalysis, where $f(x_1, x_2, \dots, x_n)$ might be a net count
 911 rate and $z_1 z_2 \dots z_m$ might be the product of the test portion size, chemical yield, counting effi-
 912 ciency, decay factor, and other sensitivity factors.

913 **EXAMPLE:** Consider the preceding gross-alpha example. Equation 19.15 implies the following
 914 equation for the combined variance of A .

$$u_c^2(A) = \frac{u_c^2(N_S / t_S - N_B / t_B)}{\epsilon^2 V^2} + A^2 \left(\frac{u^2(\epsilon)}{\epsilon^2} + \frac{u^2(V)}{V^2} \right)$$

$$= \frac{u^2(N_S) / t_S^2 + u^2(N_B) / t_B^2}{\epsilon^2 V^2} + A^2 \left(\frac{u^2(\epsilon)}{\epsilon^2} + \frac{u^2(V)}{V^2} \right)$$

916 Then, since $u^2(N_S) = N_S$ and $u^2(N_B) = N_B$,

$$u_c^2(A) = \frac{N_S / t_S^2 + N_B / t_B^2}{\epsilon^2 V^2} + A^2 \left(\frac{u^2(\epsilon)}{\epsilon^2} + \frac{u^2(V)}{V^2} \right)$$

918 19.5.4 The Estimated Covariance of Two Output Estimates

919 Measured values obtained from two measurement processes may be correlated if some of the
 920 same input estimates are used to calculate output estimates in both models. If the two measured
 921 values are to be used as input quantities in a third model, their covariance must be estimated.

922 Suppose the combined set of input quantities in two mathematical models consists of $X_1, X_2, \dots,$
 923 X_N . Then the models can be expressed as $Y = f(X_1, X_2, \dots, X_N)$ and $Z = g(X_1, X_2, \dots, X_N)$, where each
 924 of the measurands may actually depend on only a subset of the combined list of input quantities.
 925 If the input estimates are x_1, x_2, \dots, x_N and the output estimates are $y = f(x_1, x_2, \dots, x_N)$ and $z =$
 926 $g(x_1, x_2, \dots, x_N)$, the covariance of y and z is estimated by

$$u(y, z) = \sum_{i=1}^N \sum_{j=1}^N \frac{\partial y}{\partial x_i} \frac{\partial z}{\partial x_j} u(x_i, x_j) \quad (19.16)$$

927 Since $u(y, y) = u_c^2(y)$, the preceding equation may be considered a generalization of the uncertainty
 928 propagation formula.⁴

929 19.5.5 Nonlinear Models

930 19.5.5.1 Uncertainty Propagation

931 The uncertainty propagation formula tends to give better variance estimates when the function f
 932 is linear, because the formula is derived from a linear approximation of f (i.e., a first-order Taylor
 933 polynomial). Generally, obtaining a reliable estimate of $u_c^2(y)$ using the uncertainty propagation
 934 formula requires (at least) that whenever f is nonlinear in one of the input quantities X_i , the rela-
 935 tive uncertainty of the input estimate x_i must be small.⁵ In radiochemistry this rule applies, for
 936 example, to the uncertainty of an instrument calibration factor, chemical yield, or test portion
 937 size.

938 If all the input estimates x_i are uncorrelated and distributed symmetrically about their means, a
 939 better approximation of $u_c^2(y)$ may be made by including higher-order terms in the uncertainty
 940 propagation formula, as shown below.

⁴ The uncertainty propagation formula may also be generalized using the matrix notation of Attachment 19B. If $\mathbf{y} = \mathbf{f}(\mathbf{x})$, where \mathbf{x} and \mathbf{y} are column vectors and \mathbf{f} is a vector-valued function, then

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

This formula describes how the variances and covariances of the vector components of \mathbf{y} are related to the variances and covariances of the vector components of \mathbf{x} . When \mathbf{y} has only one component, the formula here is equivalent to the uncertainty propagation formula.

⁵ The uncertainty propagation formula also provides finite estimates of variance in cases where, strictly speaking, the true variance is infinite or undefined. For example, if x has a normal or Poisson distribution, the variance of $1/x$ is undefined, although the formula provides a finite estimate of it. On the other hand, if the relative standard uncertainty of x is small, the combined variance $u_c^2(1/x)$ will almost always be consistent with observation, making the estimate useful in practice.

$$u_c^2(y) = \sum_{i=1}^N \left(\frac{\partial y}{\partial x_i} \right)^2 u^2(x_i) + \sum_{i=1}^N \sum_{j=1}^N \left(\frac{1}{2} \left(\frac{\partial^2 y}{\partial x_i \partial x_j} \right)^2 + \frac{\partial y}{\partial x_i} \frac{\partial^3 y}{\partial x_i \partial x_j^2} \right) u^2(x_i) u^2(x_j) \quad (19.17)$$

941 See also Section 5.1.2 of the *GUM*.

942 **EXAMPLE:** Suppose x and y are independent estimates of input quantities X and Y , respec-
 943 tively. Then the combined variance of the product $p = xy$ according to the (first-order)
 944 uncertainty propagation formula is

$$945 \quad u_c^2(p) = y^2 u^2(x) + x^2 u^2(y)$$

946 For example, suppose $x = 5$, with $u(x) = 0.5$, and $y = 10$, with $u(y) = 1$. Then $p = 50$, and the
 947 first-order formula gives the combined standard uncertainty

$$948 \quad u_c(p) = \sqrt{10^2 0.5^2 + 5^2 1^2} = 7.07$$

949 When higher-order terms are included,

$$950 \quad \begin{aligned} u_c^2(p) &= y^2 u^2(x) + x^2 u^2(y) + 0 \cdot u^4(x) + \frac{1}{2} u^2(x) u^2(y) + \frac{1}{2} u^2(y) u^2(x) + 0 \cdot u^4(y) \\ &= y^2 u^2(x) + x^2 u^2(y) + u^2(x) u^2(y) \end{aligned}$$

951 With numbers,

$$952 \quad u_c(p) = \sqrt{10^2 0.5^2 + 5^2 1^2 + 0.5^2 1^2} = 7.09$$

953 The combined variance of the quotient $q = x / y$ according to the first-order formula is

$$954 \quad u_c^2(q) = \frac{u^2(x)}{y^2} + q^2 \frac{u^2(y)}{y^2}$$

955 Using the same values for x and y again, $q = 0.5$ and the first-order formula gives

956
$$u_c(q) = \sqrt{\frac{0.5^2}{10^2} + 0.5^2 \frac{1^2}{10^2}} = 0.0707$$

957 When the higher-order terms are included,

958
$$\begin{aligned} \frac{\partial q}{\partial x} &= \frac{1}{y} & \frac{\partial^2 q}{\partial x^2} &= 0 & \frac{\partial^3 q}{\partial x^3} &= 0 \\ \frac{\partial q}{\partial y} &= -\frac{x}{y^2} & \frac{\partial^2 q}{\partial y^2} &= \frac{2x}{y^3} & \frac{\partial^3 q}{\partial y^3} &= -\frac{6x}{y^4} \\ \frac{\partial^2 q}{\partial x \partial y} &= -\frac{1}{y^2} & \frac{\partial^3 q}{\partial x \partial y^2} &= \frac{2}{y^3} & \frac{\partial^3 q}{\partial y \partial x^2} &= 0 \end{aligned}$$

959
$$\begin{aligned} u_c^2(q) &= \frac{u^2(x)}{y^2} + q^2 \frac{u^2(y)}{y^2} + 0 \cdot u^4(x) + \left(\frac{1}{2} \left(-\frac{1}{y^2} \right)^2 + \left(\frac{1}{y} \right) \left(\frac{2}{y^3} \right) \right) u^2(x) u^2(y) \\ &\quad + \left(\frac{1}{2} \left(-\frac{1}{y^2} \right)^2 + 0 \right) u^2(y) u^2(x) + \left(\frac{1}{2} \left(\frac{4x^2}{y^6} \right) + \left(-\frac{x}{y^2} \right) \left(-\frac{6x}{y^4} \right) \right) u^4(y) \\ &= \frac{u^2(x)}{y^2} \left(1 + 3 \frac{u^2(y)}{y^2} \right) + q^2 \frac{u^2(y)}{y^2} \left(1 + 8 \frac{u^2(y)}{y^2} \right) \end{aligned}$$

960 With numbers,

961
$$u_c(q) = \sqrt{\frac{0.5^2}{10^2} \left(1 + 3 \frac{1^2}{10^2} \right) + 0.5^2 \frac{1^2}{10^2} \left(1 + 8 \frac{1^2}{10^2} \right)} = 0.0726$$

962 19.5.5.2 Bias

963 If f is nonlinear, its nonlinearity may also tend to bias the output estimate y . The bias may be esti-
964 mated, if necessary, by the formula

$$\text{Bias}(y) \approx \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{\partial^2 y}{\partial x_i \partial x_j} u(x_i, x_j) \quad (19.18)$$

965 which, in practice, is equivalent to

$$\text{Bias}(y) \approx \frac{1}{2} \sum_{i=1}^N \frac{\partial^2 y}{\partial x_i^2} u^2(x_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{\partial^2 y}{\partial x_i \partial x_j} u(x_i, x_j) \quad (19.19)$$

966 This bias is usually negligible in comparison to the combined standard uncertainty $u_c(y)$ if the
967 relative standard uncertainty of each input estimate is small.

968 **EXAMPLE:** If x is an estimate of a positive quantity X , the bias of $y = 1/x$ as an estimate of
969 $1/X$ may be approximated using Equation 19.19. Since y is a function of only one variable,
970 the partial derivatives of y are the same as ordinary derivatives. The first derivative is $dy/dx =$
971 $-x^{-2}$ and the second derivative is $d^2y/dx^2 = 2x^{-3}$. So the bias due to nonlinearity can be esti-
972 mated as $\text{Bias}(y) \approx (1/2)(2x^{-3})u^2(x) = u^2(x)/x^3$. The combined variance of y given by the
973 uncertainty propagation formula is $u_c^2(y) = (-x^{-2})^2 u^2(x) = u^2(x)/x^4$. So, the ratio of the bias to
974 the combined standard uncertainty can be estimated as $(u^2(x)/x^3) / (u(x)/x^2) = u(x)/x$,
975 which is approximately the same as the relative standard uncertainty of x . Therefore, the size
976 of the relative standard uncertainty gives an indication of the practical significance of the bias.

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

$$979 \quad \text{Bias}(z) \approx \frac{1}{2} \left(\frac{\partial^2 z}{\partial x^2} u^2(x) + \frac{\partial^2 z}{\partial y^2} u^2(y) \right)$$

980 which equals zero, since $\partial^2 z / \partial x^2 = \partial^2 z / \partial y^2 = 0$.

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

$$984 \text{Bias}(d) \approx \frac{1}{2} \frac{\partial^2 d}{\partial t^2} u^2(t) = \frac{1}{2} \lambda^2 e^{-\lambda t} u^2(t)$$

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

$$989 \frac{1}{2} (0.112707)^2 (2)^2 = 0.025$$

990 or 2.5%. Note that the relative bias of d is small if $u^2(t) / t_{1/2}^2$ is small.

991 19.5.5.3 Nominal Values

992 Sometimes an input estimate x_i is a nominal value and not the result of a measurement. This may
993 be true for example when an analyst uses a pipet to dispense a predetermined amount of tracer
994 into a sample. In this case the input estimate x_i is the predetermined volume. Since x_i never
995 varies, its variance is zero, but the volume of liquid dispensed varies each time the measurement
996 is repeated. So, the final result does have a variance component associated with the pipet. If the
997 tracer is used to measure the yield for a chemical separation, the value x_i appears as a factor in the
998 denominator of a mathematical expression, but the variable factor in that expression is actually
999 the count rate produced by the tracer, which appears in the numerator. The variance of this count
1000 rate is increased by the variability of the tracer volume. The first-order uncertainty propagation
1001 formula gives the same result for the uncertainty of the yield regardless of whether the nominal
1002 value or the true value is assumed to be variable, but the higher-order formula may not.

1003 When nominal values appear in the calculation, one must also be careful when applying the bias
1004 formula. For example, the quotient x / y may be biased if y is the result of a measurement, but it
1005 is not inherently biased if y is a nominal value.

1006 **EXAMPLE:** Suppose the measurement model is

$$1007 \quad X = \frac{Y - B}{a}$$

1008 where Y is the gross signal, B is the blank signal, and a is the nominal value for a randomly
 1009 varying sensitivity factor A , whose true value is always unknown. Suppose Y can be written in
 1010 the form $Y = xA + b + \varepsilon_Y$; where x is the true value of the measurand; b is the true blank level;
 1011 and ε_Y denotes the measurement error of Y . If all the measured (and nominal) values are
 1012 unbiased (i.e., if $E(A) = a$, $E(B) = b$, and $E(\varepsilon_Y) = 0$), then the mean of X is given by

$$1013 \quad E(X) = \frac{E(Y) - E(B)}{a} = \frac{(xa + b + 0) - b}{a} = x$$

1014 So, X is an *unbiased* estimator for x . If one treats a as a random variable, this chapter's bias-
 1015 approximation formula gives the incorrect value $Xu^2(a) / a^2$ for the bias of X .

1016 Assume A , B , and ε_Y are uncorrelated. Then the variance of Y is the sum of two components
 1017 $\sigma_{\varepsilon_Y}^2$ and $x^2\sigma_A^2$, which may be estimated by $u^2(\varepsilon_Y)$ and $X^2u^2(a)$, respectively, where $u^2(a)$ is
 1018 actually an estimate of the variance of A . The combined variance of X is given by

$$1019 \quad u_c^2(X) = \frac{u^2(Y) + u^2(B)}{a^2} = \frac{u^2(\varepsilon_Y) + X^2u^2(a) + u^2(B)}{a^2}$$

1020 The expression on the right may be obtained from the first-order uncertainty propagation
 1021 formula even if one incorrectly treats a as a random variable and A as a constant, so that
 1022 $u^2(Y) = u^2(\varepsilon_Y)$. If the higher-order approximation is used, the same expression is obtained only
 1023 if one correctly treats a as the constant and A as the random variable.

1024 **19.6 Radiation Measurement Uncertainty**

1025 **19.6.1 Radioactive Decay**

1026 Although it is impossible to know when an unstable nucleus will decay, it is possible to calculate
 1027 the probability of decay during a specified time interval. The lifetime of the nucleus has an

1028 *exponential distribution*, which is a model for the life of any object whose expected remaining
 1029 life does not change with age.

1030 The exponential distribution is described by one parameter λ , which measures the expected frac-
 1031 tional decay rate. This parameter λ is called the *decay constant* and equals $\ln 2 / t_{1/2}$, or approx-
 1032 imately $0.693 / t_{1/2}$, where $t_{1/2}$ is the half-life of the radionuclide (sometimes denoted by $T_{1/2}$). The
 1033 half-life is the same as the median of the exponential distribution.

1034 The probability that an atom will survive until time t without decaying is equal to $e^{-\lambda t}$. Thus the
 1035 probability of survival decreases exponentially with time. Consequently, when a large number of
 1036 atoms of the same radionuclide are considered, the expected number of surviving atoms also
 1037 decreases exponentially with time, as shown in Figure 19.4.

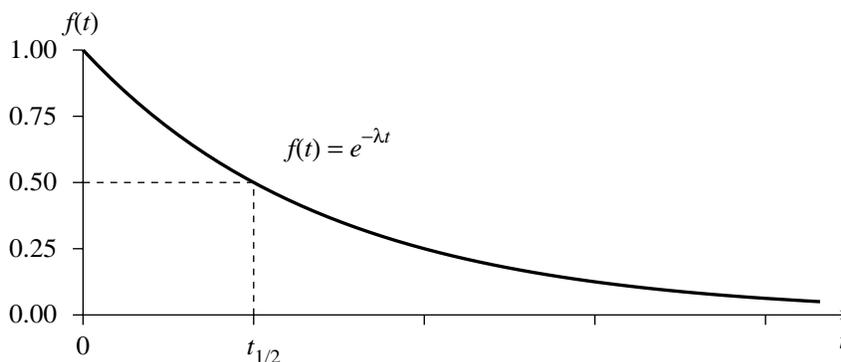


FIGURE 19.4 — Expected fraction of atoms remaining at time t

1038 Since the probability that an atom survives until time t is equal to $e^{-\lambda t}$, it follows that the
 1039 probability of decay during this time is $1 - e^{-\lambda t}$.

1040 **19.6.2 Radiation Counting**

1041 Undoubtedly the best-known rule of radiation measurement statistics is the fact that the counting
 1042 uncertainty for a gross radioactivity measurement can be evaluated as the square root of the
 1043 observed counts. The square-root rule is useful, because it permits the estimation of a potentially
 1044 significant uncertainty component without replicate measurements. Although the rule is usually
 1045 valid as an approximation, for reasons which are discussed below, there are limits to its applica-
 1046 bility. It is also important to remember that the counting uncertainty is only one component of the
 1047 total measurement uncertainty.

1048 When a source containing a radionuclide is placed in a detector, the probability that a particular
 1049 atom of the radionuclide will produce a count is the product of three factors: the probability of
 1050 decay (nuclear transformation), the probability of emission of the radiation being measured, and
 1051 the probability of detection. According to the exponential decay model, the probability of decay
 1052 is equal to $1 - e^{-\lambda t}$, where λ is the decay constant and t is the counting time. The probability of
 1053 radiation emission, denoted here by F , is a characteristic of the radionuclide. The probability of
 1054 detection is the same as the counting efficiency ϵ . Then the probability that an atom will generate
 1055 a count is $p = (1 - e^{-\lambda t})F\epsilon$.

1056 If the source initially contains n atoms of the radionuclide, the instrument is stable, and its back-
 1057 ground is negligible, the number of observed counts N has a *binomial distribution with param-*
 1058 *eters n and p* . In general, if an experiment has only two possible outcomes, which may be called
 1059 “success” and “failure,” and the probability of success is p , then the number of successes
 1060 observed when the experiment is repeated in n independent trials has a binomial distribution with
 1061 parameters n and p .

1062 Actually the probability p is a random variable, because the counting efficiency for an instrument
 1063 and source can vary for a number of reasons, such as source placement, dead time, and other
 1064 instrument characteristics. These variations generate measurement uncertainty, but their effects
 1065 are not included in the “counting uncertainty.” The counting uncertainty is the standard deviation
 1066 of the *theoretical* distribution of counts observed in a fixed time period when the efficiency is
 1067 held constant. *Thus, the actual variability observed in repeated measurements of a single radio-*
 1068 *active source may be greater than the theoretical counting uncertainty.*

1069 The mean and variance of the binomial distribution are np and $np(1 - p)$, respectively. In radi-
 1070 ation counting, the value of p is usually small enough that the factor $1 - p$ in the variance can be
 1071 ignored. When this is true, the binomial distribution can be approximated by a *Poisson distri-*
 1072 *bution* with mean $\mu = np$. The variance of a Poisson distribution equals the mean; so, both can be
 1073 estimated by the same measured result N , and the standard deviation can be estimated by \sqrt{N} .⁶

⁶ In the rare cases when the Poisson counting 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 a Poisson background is measured for time t_B and N_B counts are observed, the standard deviation of N_S should be estimated instead by

$$\sigma_{N_S} \approx \sqrt{(1-p)N_S + pN_B \frac{t}{t_B}}$$

These two expressions are appropriate only when the source counts are generated by a single radionuclide or by one radionuclide plus the instrument background.

1074 When μ is large, \sqrt{N} is an excellent estimator for the standard deviation, but the estimate may be
1075 poor when μ is small. For example, if $\mu = 100$, the coefficient of variation of \sqrt{N} is only about
1076 5% and its bias is negligible. If $\mu = 10$, the coefficient of variation is more than 16% and there is
1077 a negative bias of more than 1%. If $\mu = 1$, the coefficient of variation is more than 63% and the
1078 negative bias is more than 22%. Furthermore, when μ is small, it is possible to observe zero
1079 counts, so that $\sqrt{N} = 0$. MARLAP recommends that \sqrt{N} be replaced by $\sqrt{N + 1}$ when extremely
1080 low counts are possible (see also Attachment 19C).⁷

1081 A sum of independent Poisson quantities also has a Poisson distribution. So, when the Poisson
1082 approximation is valid for all the sources of counts in a counting measurement, the total count
1083 obeys Poisson counting statistics as well.

1084 If a short-lived radionuclide (large λ) is counted in a high-efficiency detector (large ϵ), the prob-
1085 ability p that an atom placed in the detector will produce a count may be so large that the Poisson
1086 approximation is invalid. In this case the Poisson approximation overestimates the counting
1087 uncertainty, but it is important to consider that the statistical model described thus far represents
1088 only the process of counting. In most cases previous steps in the measurement process decrease
1089 the probability that one of the atoms of interest initially present in the test portion will produce a
1090 count. If a correction for decay before counting is performed, the decay factor must be included
1091 in p . If the measured activity of a (single) decay product is used to estimate the activity of a
1092 parent, p must include both ingrowth and decay factors. If a chemical extraction is performed, the
1093 recovery factor must be considered. When these factors are included, the Poisson counting model
1094 is usually valid. Note, however, that these factors must be measured and their standard uncertain-
1095 ties evaluated and propagated, increasing the total measurement uncertainty even further.⁸

1096 Both the binomial and Poisson models may be invalid if one atom can produce more than one
1097 count during the measurement. This situation occurs when the activity of a parent is estimated
1098 from the total count produced by a series of short-lived progeny (Lucas and Woodward 1964,
1099 Collé and Kishore 1997). For example, when ²²²Rn is measured by counting the emissions of its

⁷ The negative bias of \sqrt{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.

⁸ 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.

1100 progeny, an atom of ^{222}Rn may produce several counts as it decays through the short-lived series
 1101 ^{218}Po , ^{214}Pb , ^{214}Bi , and ^{214}Po , to the longer-lived ^{210}Pb .

1102 Both counting models may also be invalid if the total dead time of the measurement is significant
 1103 (see Section 19.6.3.1).

1104 Instrument background measurements are usually assumed to follow the Poisson model. This
 1105 assumption is reasonable if the background counts are produced by low levels of relatively long-
 1106 lived radionuclides. However, the true background may vary between measurements (e.g.,
 1107 cosmic background). Furthermore, the measured background may include spurious instrument-
 1108 generated counts, which do not follow a Poisson distribution. Generally, the variance of the
 1109 observed background is somewhat greater than the Poisson counting variance, although it may be
 1110 less for certain types of instruments, such as those that use parallel coincidence counters to com-
 1111 pensate for background instability (Currie et al. 1998). Departures from the Poisson model may
 1112 be detected using the chi-square test described in Section 18B.2 of Attachment 18B; however,
 1113 deviations from the model over short time periods may be small and difficult to measure.

1114 19.6.3 Count Rate

1115 Suppose a radiation counting measurement of duration t is made for the purpose of estimating a
 1116 mean count rate R , assumed to be constant, and the result of the measurement N (in counts) has a
 1117 distribution that is approximately Poisson with mean Rt . If t is known precisely, the best estimate
 1118 of R given a single observation $N = n$ is the measured count rate $r = n / t$, and the best estimate of
 1119 the variance of the measured rate is $u^2(r) = n / t^2 = r / t$. Under the Poisson assumption, even if
 1120 repeated measurements are made, the best estimates of r and its variance are obtained by pooling
 1121 the counts and count times and using the same formulas.

1122 In fact the count time t is known imperfectly; so, a more complete estimate of the variance of r is

$$u^2(r) = \frac{n}{t^2} + \frac{n^2}{t^4} u^2(t) \quad (19.20)$$

1123 The uncertainty of t may be ignored if $u(t) / t \ll 1 / \sqrt{n}$, that is, if the relative standard uncertainty
 1124 of t is much less than 1 over the square root of the count.

1125 **EXAMPLE:** A source is counted for $t = 100$ s, where t has standard uncertainty $u(t) = 0.1$ s, and
 1126 $n = 961$ counts observed. When $u(t)$ is ignored, the combined standard uncertainty of the count
 1127 rate r is $u_c(r) = \sqrt{n/t^2}$, or 0.31 cps. When $u(t)$ is included, the combined standard uncertainty
 1128 is

$$u_c(r) = \sqrt{\frac{n}{t^2} + \frac{n^2}{t^4}u^2(t)} = \sqrt{\frac{961}{10^4} + \frac{961^2}{10^8}0.1^2} \approx 0.31 \text{ cps}$$

1130 In this case, the difference between the two uncertainty estimates is negligible.

1131 **EXAMPLE:** A source is counted for $t = 100$ s, where $u(t) = 1$ s, and $n = 10,609$ counts observed.
 1132 When $u(t)$ is ignored, $u_c(r) = \sqrt{n/t^2} = 1.03$ cps. When $u(t)$ is included,

$$u_c(r) = \sqrt{\frac{n}{t^2} + \frac{n^2}{t^4}u^2(t)} = \sqrt{\frac{10,609}{10^4} + \frac{10,609^2}{10^8}1^2} \approx 1.48 \text{ cps}$$

1134 In this example the difference between the two estimates is clearly significant.

1135 Sometimes a radiation counter is set to acquire a predetermined number of counts. In this case
 1136 the number of counts is a constant, and only the count time varies. If the mean count rate does
 1137 not change appreciably during the measurement, then Equation 19.20 may still be used.⁹

19.6.3.1 Dead Time

1139 The *dead time* for a counting instrument is the minimum separation τ between two events
 1140 required for the instrument to process and record both. Theoretical models for dead time are
 1141 generally of two types. If the dead time for one event may be extended by a second event that
 1142 arrives before the first has been processed, the system is called “paralyzable” and the dead time is
 1143 called “extendable.” Otherwise, the system is called “non-paralyzable” and the dead time is
 1144 called “non-extendable” (Knoll 1989, Turner 1995, NCRP 1985). Both models are idealized. The

⁹ 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 $\lambda = R$.

1145 behavior of an actual counting system tends to fall between the two extremes. At low count rates,
 1146 however, both models give essentially the same predictions.

1147 At low count rates the observed count rate n / t may be corrected for dead time by dividing by the
 1148 factor $1 - n\tau / t$. Many counting instruments perform the correction automatically by extending
 1149 the real time t of the measurement to achieve a desired live time t_L . Since $t_L = t - n\tau$, the correct-
 1150 ed count rate is simply n / t_L . When the dead time rate for the measurement is low, the variance
 1151 of the corrected count rate may be estimated as n / t_L^2 . Thus, the Poisson model remains adequate
 1152 if the “count time” is equated with the live time. When the dead time rate is high (above 20%),
 1153 the same estimate may not be adequate (NCRP 1985). In this case the measurement should be
 1154 repeated, if possible, in a manner that reduces the dead time rate.

1155 Dead time effects may be evaluated experimentally to confirm that they do not invalidate the
 1156 Poisson model at the count rates expected for typical measurements. The chi-square test
 1157 described in Section 18B.2 of Attachment 18B can be used for this purpose.

1158 19.6.3.2 A Confidence Interval for the Count Rate

1159 When the Poisson counting model is valid, lower and upper confidence limits for the mean count
 1160 rate R given an observation of n counts in time t may be calculated as follows:¹⁰

$$\begin{aligned} R_{\text{lower}} &= \chi_{(1-\gamma)/2}^2(2n) / 2t \\ R_{\text{upper}} &= \chi_{(1+\gamma)/2}^2(2n + 2) / 2t \end{aligned} \tag{19.21}$$

1161 Here γ is the desired *confidence coefficient*, or the minimum probability of coverage, and $\chi_p^2(n)$
 1162 denotes the p -quantile of the chi-square distribution with n degrees of freedom (see Table G.3 in
 1163 Appendix G). If $n = 0$, the chi-square distribution $\chi^2(n)$ is degenerate. For our purposes $\chi_p^2(0)$
 1164 should be considered to be 0.

¹⁰ The chi-square distribution is a special case of a gamma distribution, whose relationship to the Poisson distribu-
 tion is described by Hoel et al. (1971) and Stapleton (1995). This relationship is the basis for the two formulas in
 Equation 19.21. The relationship is such that if X is chi-square with $2n$ degrees of freedom and Y is Poisson with
 mean μ , then $\Pr[X \leq 2\mu] = \Pr[Y \geq n]$.

1165 **EXAMPLE:** Suppose 10 counts are observed during a 600-second instrument background
1166 measurement. Then the 95% confidence limits for the background count rate are

$$R_{\text{lower}} = \frac{\chi_{0.025}^2(20)}{(2)(600)} = \frac{9.59078}{1200} = 0.00799 \text{ cps}$$

$$R_{\text{upper}} = \frac{\chi_{0.975}^2(22)}{(2)(600)} = \frac{36.7807}{1200} = 0.03065 \text{ cps}$$

1168 **EXAMPLE:** Suppose 0 counts are observed during a 600-second measurement. Then the 95%
1169 confidence limits for the count rate are

$$R_{\text{lower}} = \frac{\chi_{0.025}^2(0)}{(2)(600)} = 0 \text{ cps}$$

$$R_{\text{upper}} = \frac{\chi_{0.975}^2(2)}{(2)(600)} = \frac{7.3778}{1200} = 0.00615 \text{ cps}$$

1171 19.6.4 Instrument Background

1172 As noted above, single-channel background measurements are usually assumed to follow the
1173 Poisson model, although there may be effects which increase the variance beyond what the model
1174 predicts. For example, the cosmic radiation and other natural sources of instrument background
1175 may vary between measurements, the composition of source holders and containers may vary, the
1176 instrument may become contaminated by sources, or the instrument may be unstable. For certain
1177 types of instruments, the Poisson model may overestimate the background variance (Currie et al.
1178 1998). If the background does not closely follow the Poisson model, its variance should be esti-
1179 mated by repeated measurements.

1180 The “instrument background,” or “instrument blank,” is usually measured with source holders or
1181 containers in place, since the presence of the container may affect the count rate. In many cases,
1182 perhaps most, it is not feasible to use the same container during both the background and test
1183 source measurements, but nearly identical containers should be used. Variations in container
1184 composition may affect the background count rate. If test sources contain enough mass to atten-
1185 uate background radiation, then it is best to use a similar amount of blank material during the
1186 background measurement.

1187 If repeated measurements demonstrate that the background level is stable, then the average \bar{x} of
 1188 the results of many similar measurements performed over a period of time may give the best
 1189 estimate of the background. In this case, if all measurements have the same duration, the experi-
 1190 mental standard deviation of the mean $s(\bar{x})$ is also a good estimate of the measurement uncer-
 1191 tainty. Given the Poisson assumption, the best estimate of the uncertainty is still the Poisson
 1192 estimate, which equals the square root of the summed counts, divided by the number of measure-
 1193 ments, but the experimental standard deviation may be used when the Poisson assumption is
 1194 false.

1195 If the background drifts or varies nonrandomly over time (i.e., is nonstationary), it is important to
 1196 minimize the consequences of the drift by performing frequent blank measurements.

1197 If the background variance includes a small non-Poisson component, that component can be esti-
 1198 mated from historical background data and added to the calculated Poisson component. A chi-
 1199 square statistic may be used to detect and quantify non-Poisson background variance (Currie
 1200 1972; see also Section 18B.3 of Attachment 18B), but chi-square provides an unbiased estimate
 1201 of the additional variance only if the background remains stationary while the data are being
 1202 collected. If the observed background counts, in order, are N_1, N_2, \dots, N_n and the corresponding
 1203 counting intervals are t_1, t_2, \dots, t_n , then the quantity

$$\xi_B^2 = \frac{1}{n-1} \left[\sum_{i=1}^{n-1} \left(\frac{N_{i+1}}{t_{i+1}} - \frac{N_i}{t_i} \right)^2 - \frac{\sum_{i=1}^n N_i}{\sum_{i=1}^n t_i} \sum_{i=1}^{n-1} \left(\frac{1}{t_{i+1}} + \frac{1}{t_i} \right) \right] \quad (19.22)$$

1204 may be used to estimate the non-Poisson variance of a net count rate due to background even if
 1205 the background is not stationary. The distribution of ξ_B^2 is not simple, and ξ_B^2 may even assume
 1206 negative values, which are clearly unrealistic. So, if this estimator is used, it should be calculated
 1207 for several data sets and for more than one instrument, if possible, to give an indication of its
 1208 reliability. Although replicate measurements are involved, this type of evaluation of uncertainty
 1209 should be considered a Type B method.

1210 If background and test source measurements are performed under different conditions, the back-
 1211 ground measurement may be biased. Such a bias may occur, for example, if test sources are
 1212 counted in containers or on planchets which are not present during background measurements. A
 1213 situation of this kind should be avoided if possible.

1214 When instrument background levels are low or when count times are short, it is possible that too
1215 few counts will be observed to provide an accurate estimate of the measurement uncertainty.
1216 Attachment 19C describes a method for choosing an appropriate coverage factor when only few
1217 counts are observed.

1218 **19.6.5 Counting Efficiency**

1219 The counting efficiency for a measurement of radioactivity may depend on many factors, includ-
1220 ing source geometry, placement, composition, density, activity, radiation type and energy, and
1221 other instrument-specific factors. The estimated efficiency is sometimes calculated explicitly as a
1222 function of such variables (in gamma spectrometry, for example). In other cases a single meas-
1223 ured value is used (e.g., alpha spectrometry). If an efficiency function is used, the uncertainties of
1224 the input estimates, including those for both calibration parameters and sample-specific quanti-
1225 ties, must be propagated to obtain the combined standard uncertainty of the estimated efficiency.
1226 Calibration parameters tend to be correlated; so, estimated covariances must also be included. If
1227 a single value is used instead of a function, the standard uncertainty of the value is determined
1228 when the value is measured.

1229 **EXAMPLE**

1230 Several sources with the same geometry are prepared and used to calibrate a radiation counter.
1231 One blank measurement is made. Each source is counted once to obtain an estimate of the
1232 count rate, the estimates are averaged, and the average is used to calculate the counting
1233 efficiency. The sources are long-lived and all source count times are equal. Let

1234	C	= concentration of standard solution ($C = 1500$, $u(C) = 20 \text{ Bq g}^{-1}$)
1235	M	= mean mass of solution added to each source (0.09980 g, added by a 0.1-mL pipet)
1236	n	= number of sources (15)
1237	N_B	= blank count (90)
1238	t_S	= source count time (300 s)
1239	t_B	= blank count time (6000 s)
1240	$N_{S,i}$	= gross count observed during the measurement of the i^{th} source
1241	R_i	= gross count rate observed in the i^{th} source measurement
1242	\bar{R}	= arithmetic mean of the gross count rates, R_i
1243	ϵ	= estimated counting efficiency

1244 Then the following equations may be used to calculate the mean efficiency and its standard
1245 uncertainty:

$$R_i = \frac{N_{S,i}}{t_S}, \quad i = 1, 2, \dots, n$$

$$\bar{R} = \frac{1}{n} \sum_{i=1}^n R_i$$

1246
$$s^2(\bar{R}) = \frac{1}{n(n-1)} \sum_{i=1}^n (R_i - \bar{R})^2$$

$$\varepsilon = \frac{\bar{R} - N_B / t_B}{CM}$$

$$u(\varepsilon) = \sqrt{\frac{s^2(\bar{R}) + N_B / t_B^2}{C^2 M^2} + \varepsilon^2 \left(\frac{u^2(C)}{C^2} + \frac{u^2(M)}{M^2} \right)}$$

1247 The source-to-source variability of the mass M is not explicitly evaluated, because it is
1248 included in the observed variability of the count rates, R_i . So, the standard uncertainty $u(M)$
1249 represents only the uncertainty of the mean mass added by the pipet. This uncertainty arises
1250 from uncertainty in the capacity of the pipet, the density of the solution, temperature effects,
1251 and the analyst's technique. Assume for this example that $u(M)$ is 0.00050 g (about 0.5%).

1252 Note that the uncertainty of the blank count, N_B , is negligible in this example and could have
1253 been ignored. It was included only for completeness.

1254 Assume the observed source counts, $N_{S,i}$, are as follows:

1255	15,708	15,946	15,953	16,012	16,066
1256	15,924	15,844	16,020	15,877	16,061
1257	16,120	15,902	16,211	16,181	15,984

1258 Then the observed gross count rates, R_i , are:

1259	52.360	53.153	53.177	53.373	53.553
1260	53.080	52.813	53.400	52.923	53.537
1261	53.733	53.007	54.037	53.937	53.280

1262 The average of the gross count rates is calculated as follows.

1263
$$\bar{R} = \frac{1}{15} \sum_{i=1}^{15} R_i = \frac{799.363}{15} = 53.2909$$

1264 The experimental variance of \bar{R} is

1265
$$s^2(\bar{R}) = \frac{1}{15(15-1)} \sum_{i=1}^{15} (R_i - 53.2909)^2 = 0.012876$$

1266 Then the estimated counting efficiency is

1267
$$\varepsilon = \frac{53.2909 - 90 / 6000}{(1500)(0.09980)} = 0.355884$$

1268 and the standard uncertainty of ε is given by

1269
$$u(\varepsilon) = \sqrt{\frac{0.012876 + 90 / 6000^2}{(1500)^2 (0.09980)^2} + 0.355884^2 \left(\frac{20^2}{1500^2} + \frac{0.0005^2}{0.09980^2} \right)} = 0.0051$$

1270 In fact, the standard uncertainty of ε calculated in the preceding example may be incomplete. The
 1271 true counting efficiency may vary from source to source because of variations in geometry, posi-
 1272 tion, and other influence quantities not explicitly included in the model. So, the standard uncer-
 1273 tainty of ε should include not only the standard uncertainty of the estimated mean, as calculated
 1274 in the example, but also a second component of uncertainty due to variations of the true effi-
 1275 ciency during subsequent measurements. The second component may be written as $\varepsilon^2 \varphi^2$, where φ
 1276 is an estimate of the coefficient of variation of the true efficiency. Then the standard uncertainty
 1277 of ε equals the square root of the sum of the squares of the two components.

1278 In the example above, the experimental variance of the count rates, $s^2(R_i)$, might be used to esti-
 1279 mate φ^2 . Procedure E2, which is described in Section 18B.2 of Attachment 18B, is a step-by-step
 1280 procedure for estimating such “excess” variance in a series of measurements. However, if the
 1281 procedure were applied to the series of measurements made in the example, the estimated vari-
 1282 ance might be inflated by errors in the pipetting of the standard solution. The resulting estimate

1283 would therefore tend to be an upper bound. A lower bound for the excess variance could be esti-
1284 mated by making replicate measurements of only one source, thus eliminating the effects of
1285 pipetting errors but also unfortunately eliminating the effects of variable source geometry. A
1286 better approach is to weigh the amount of standard solution added to each source, use the results,
1287 M_i , to calculate 15 individual estimates of the counting efficiency, ϵ_i , and estimate the excess
1288 variance of the values ϵ_i .

1289 Variations in counting efficiency due to source placement should be reduced as much as possible
1290 through the use of positioning devices that ensure a source with a given geometry is always
1291 placed in the same location relative to the detector. If such devices are not used, variations in
1292 source position may significantly increase the measurement uncertainty.

1293 Calibrating an instrument under conditions different from the conditions under which test sources
1294 are counted may lead to large uncertainties in the sample activity measurements. Source geome-
1295 try in particular tends to be an important factor for many types of radiation counting instruments.
1296 Generally, calibration sources should be prepared with the sizes and shapes of test sources and
1297 counted in the same positions, although in some cases it may be possible to calculate correction
1298 factors which allow one calibration to be used for different geometries. When correction factors
1299 are used, their uncertainties should be evaluated and propagated.

1300 If the efficiency ϵ is calculated from a model that includes one of the quantities X_i appearing else-
1301 where in the sample activity model, there is a correlation between the measured values of ϵ
1302 and X_i , which should not be ignored. It is often simpler to include the entire expression for ϵ
1303 in the expression for the laboratory sample activity before applying the uncertainty propagation
1304 formula.

1305 **EXAMPLE:** Suppose the counting efficiency for a measurement is modeled by the equation
1306 $\epsilon = A \exp(-B M_S)$, where A and B are calibration parameters and M_S is the source mass; and
1307 suppose the chemical yield Y is modeled by M_S / M_C , where M_C is the expected mass at 100%
1308 recovery. Then the estimated values of the counting efficiency and the yield are correlated,
1309 because both are calculated from the same measured value of the source mass. When the com-
1310 bined standard uncertainty of the sample activity is calculated, the covariance $u(\epsilon, Y)$ may be
1311 included in the uncertainty propagation formula, or the variables ϵ and Y in the model may be
1312 replaced by the expressions $A \exp(-B M_S)$ and M_S / M_C , respectively.

1313 In some cases the estimated value of the counting efficiency has *no effect* on the output estimate
1314 of laboratory sample activity. This happens often in alpha spectrometry, for example, when iso-
1315 topic tracers are used. The efficiency estimate is needed to obtain an estimate of the yield of the

1316 chemistry procedure, but the efficiency usually cancels out of the mathematical model for the
1317 laboratory sample activity and its uncertainty is not propagated when determining the combined
1318 standard uncertainty of the activity estimate.

1319 **19.6.6 Radionuclide Half-life**

1320 The component of combined standard uncertainty associated with the half-life of a radionuclide
1321 is often negligible in measurements performed by typical radioanalytical laboratories, since the
1322 half-lives of most radionuclides of interest have been measured very accurately and in many
1323 cases decay times are short relative to the half-life (so that the sensitivity coefficient is small).
1324 However, this uncertainty component is also one of the most easily obtained components, since
1325 radionuclide half-lives and their standard uncertainties are evaluated and published by the
1326 National Nuclear Data Center (NNDC) at Brookhaven National Laboratory. The data may be
1327 obtained from the NNDC website (www.nndc.bnl.doe.gov).

1328 **19.6.7 Gamma Spectrometry**

1329 There are a number of sources of measurement uncertainty in gamma spectrometry, including:

- 1330 • Poisson counting uncertainty
- 1331 • Compton baseline determination
- 1332 • Background peak subtraction
- 1333 • Multiplets and interference corrections
- 1334 • Peak-fitting model errors
- 1335 • Efficiency calibration model error
- 1336 • Summing
- 1337 • Density correction factors
- 1338 • Dead time

1339 See Chapter 17 for further discussion of measurement models and uncertainty analysis for
1340 gamma spectrometry.

1341 **19.6.8 Balances**

1342 The uncertainty of a balance measurement tends to be small, even negligible, when the balance is
1343 used properly and the mass being measured is much larger than the balance's readability. How-
1344 ever, the uncertainty may also be difficult to evaluate unless the balance is well maintained and
1345 operated in a controlled environment that protects it from external influences. In particular, drafts

1346 or sudden changes in pressure, temperature or humidity (e.g., opening doors or dishwashers) may
1347 produce spurious errors.

1348 The uncertainty of the result of a balance measurement generally has components associated with
1349 balance calibration, linearity, repeatability, day-to-day variability due to environmental factors,
1350 and air buoyancy. Other sources of uncertainty may include leveling errors and off-center errors,
1351 which should be controlled. Static electrical charges may also have an effect. For some materials,
1352 gain or loss of mass before or after weighing (e.g., by absorption or evaporation of water) may be
1353 significant. Attachment 19G of this chapter describes several of these uncertainty components in
1354 more detail.

1355 Balance manufacturers provide specifications for repeatability and linearity, which are usually of
1356 the same order of magnitude as the balance's readability, but tests of repeatability and linearity
1357 should also be included in the routine quality control for the balance.

1358 Repeatability is expressed as a standard deviation and is typically assumed to be independent of
1359 the load. It represents the variability of the result of zeroing the balance, loading and centering a
1360 mass on the pan, and reading the final balance indication.

1361 The linearity tolerance of a balance, a_L , should be specified by the manufacturer as the maximum
1362 deviation of the balance indication from the value that would be obtained by linear interpolation
1363 between the calibration points. Different methods may be used to convert this tolerance to a
1364 standard uncertainty, depending on the form the linearity error is assumed to take. One method,
1365 which is recommended by the *Eurachem/CITAC Guide: Quantifying Uncertainty in Analytical*
1366 *Measurement*, is to treat the tolerance, a_L , as the half-width of a rectangular distribution and
1367 divide a_L by $\sqrt{3}$ to obtain the standard uncertainty (Eurachem 2000). Another method, suggested
1368 in Attachment 19G of this chapter, is to treat a_L as the amplitude of a sinusoidal function. This
1369 model requires that a_L be divided by $\sqrt{2}$ to obtain the standard uncertainty. The latter method is
1370 used below.

1371 Procedures for evaluating the relative standard uncertainties due to calibration and environmental
1372 factors and for calculating the buoyancy correction factor and its standard uncertainty are
1373 described in Attachment 19G.

1374 A typical mass measurement in the laboratory involves separate measurements of a gross mass
1375 and a tare mass. The net mass, m , is determined by subtracting the balance indication for the tare
1376 mass, I_{Tare} , from the indication for the gross mass, I_{Gross} , and multiplying the difference, I_{Net} , by
1377 the buoyancy correction factor, B . That is,

$$m = I_{\text{Net}} B = (I_{\text{Gross}} - I_{\text{Tare}}) B \quad (19.23)$$

1378 The standard uncertainty of m is given by

$$u(m) = \sqrt{B^2 (I_{\text{Net}}^2 (\phi_{\text{Cal}}^2 + \phi_{\text{Env}}^2) + a_L^2 + 2s_r^2) + I_{\text{Net}}^2 u^2(B)} \quad (19.24)$$

1379 where

- 1380 m is the buoyancy-corrected net mass
- 1381 I_{Net} is the net balance indication ($I_{\text{Gross}} - I_{\text{Tare}}$)
- 1382 I_{Tare} is the balance indication for the tare mass
- 1383 I_{Gross} is the balance indication for the gross mass
- 1384 B is the buoyancy correction factor

1385 Attachment 19G describes uncertainty equations for use in other circumstances.

1386 **19.6.9 Pipets and Other Volumetric Apparatus**

1387 Generally, a pipet or volumetric flask is used not to measure an existing volume of liquid, but to
 1388 obtain a volume of a predetermined nominal size. The nominal value is treated as if it were a
 1389 measured value, although it is known before the “measurement.” The true volume is the variable
 1390 quantity. Since a volumetric “measurement” of this type cannot be repeated, pipets and flasks are
 1391 good examples of measurement systems for which historical data are important for Type A eval-
 1392 uations of standard uncertainty.

1393 The density of a liquid depends on its temperature. For this reason, when a volume is being
 1394 measured, one should determine whether the volume of interest is the volume at the current room
 1395 temperature, the long-term mean room temperature, or some other temperature, such as 20°C.
 1396 One should also determine whether the effect of temperature is significant for the measurement.
 1397 Often it is not, but in some cases a correction for thermal expansion may be necessary.

1398 The standard uncertainty for a volumetric measurement includes components associated with the
 1399 capacity of the measuring device, temperature effects, repeatability, and the analyst’s bias in
 1400 using the device (e.g., reading a meniscus).

1401 The capacity of a volumetric pipet or flask (at 20°C) is generally specified with a tolerance a ,
 1402 which may be assumed to represent the half-width of a triangular distribution (e.g., see ASTM

1403 1994 and ASTM 1995). Assuming a triangular distribution, one evaluates the uncertainty com-
1404 ponent of the volume associated with the capacity as $a / \sqrt{6}$.

1405 The relative standard uncertainty due to temperature variations is typically a Type B standard
1406 uncertainty, which may be derived from a temperature range, $T \pm \delta T$, and the liquid's coefficient
1407 of thermal expansion, β , at the center of the range. Assuming a rectangular distribution for the
1408 temperature with half-width δT , the relative standard uncertainty component due to temperature
1409 variations is $|\beta| \delta T / \sqrt{3}$.

1410 The nominal capacity of any volumetric glassware is usually specified at 20°C. If the glassware
1411 is used at a different temperature, the capacity is slightly different. Temperature effects on the
1412 capacity are generally very small (much smaller than the effects on the density of the liquid) and
1413 for this reason one may usually ignore them. The relationship between the capacity and the
1414 temperature is given approximately by

$$V_T = V_{20} (1 + \alpha(T - 20)) \quad (19.25)$$

1415 where

1416 T is the temperature (°C)
1417 V_T is the capacity at temperature T
1418 V_{20} is the capacity at 20°C
1419 α is the glassware's coefficient of thermal cubical expansion (°C⁻¹)

1420 The value of α for ASTM Type I, Class A, borosilicate glassware is approximately 0.00001 °C⁻¹;
1421 so, the capacity increases by only about 0.001% for each degree Celsius of temperature increase.

1422 An analyst may calibrate a pipet gravimetrically using an analytical balance. The balance, to be
1423 useful, must provide better accuracy than the pipet. In particular, the balance's repeatability and
1424 linearity tolerance should be small relative to the tolerances for the pipet. The calibration pro-
1425 vides an estimate of the pipet's capacity, the standard uncertainty of the capacity, and the var-
1426 iability to be expected during use. The procedure involves dispensing a series of n pipet volumes
1427 of a specified liquid into a container and weighing the container and zeroing the balance after
1428 each volume is added. Usually the container must have a small mouth to reduce evaporation. The
1429 temperature of the room, the liquid, and the apparatus involved should be specified, equilibrated,
1430 and controlled during the experiment.

1431 The procedure produces a set of balance indications, I_i , which are averaged to obtain the arith-
1432 metic mean \bar{I} . To obtain the estimated mean pipet volume, v , the mean balance indication, \bar{I} , is

1433 multiplied by a factor Z , which equals the quotient of the buoyancy correction factor divided by
 1434 the density of the liquid at room temperature. A correction factor for thermal expansion of the
 1435 pipet may also be included, if necessary.

$$v = \bar{V}Z \quad \text{where} \quad Z = \frac{1 - \rho_{A,C} / \rho_C}{\rho_M - \rho_{A,M}} \quad (19.26)$$

1436 and where

- 1437 ρ_M is the density of the liquid
- 1438 $\rho_{A,M}$ is the density of the air at the time the liquid is weighed
- 1439 ρ_C is the density of the calibration mass standard for the balance
- 1440 $\rho_{A,C}$ is the density of the air at the time of the balance calibration

1441 The calibration is most often performed using water.

1442 ASTM E542, “Standard Practice for Calibration of Laboratory Volumetric Apparatus,” provides
 1443 additional information about the procedure, including tables of values of Z for various conditions
 1444 (ASTM 2000). Table 19.2, which is taken from ASTM E542, shows the density of air-free water
 1445 at various temperatures. Attachment 19G of this chapter describes an equation to calculate the
 1446 density of air as a function of temperature, pressure, and humidity.

TABLE 19.2 — Density of air-free water

Temperature, °C	Density, g/cm ³	Temperature, °C	Density, g/cm ³
15	0.999098	26	0.996782
16	0.998941	27	0.996511
17	0.998773	28	0.996232
18	0.998593	29	0.995943
19	0.998403	30	0.995645
20	0.998202	31	0.995339
21	0.997990	32	0.995024
22	0.997768	33	0.994701
23	0.997536	34	0.994369
24	0.997294	35	0.994030
25	0.997043		

1447 The volume, v , estimated by the calibration may be substituted for the pipet's nominal capacity
 1448 when the pipet is used later in an analytical measurement. The uncertainty of v as an estimate of
 1449 the mean volume may be calculated as follows.

$$\begin{aligned}
 u(\bar{I}Z) &= \sqrt{Z^2 u^2(\bar{I}) + \bar{I}^2 u^2(Z)} \\
 &= \sqrt{Z^2 (s^2(\bar{I}) + \bar{I}^2 (\varphi_{\text{Cal}}^2 + \varphi_{\text{Env}}^2)) + \bar{I}^2 u^2(Z)} \\
 &= \sqrt{Z^2 \frac{s^2(I_i)}{n} + v^2 \left(\varphi_{\text{Cal}}^2 + \varphi_{\text{Env}}^2 + \frac{\beta^2 \delta T^2}{3} \right)}
 \end{aligned}
 \tag{19.27}$$

1450 where φ_{Cal} and φ_{Env} denote the relative standard uncertainties of mass measurements associated
 1451 with balance calibration and environmental factors, respectively (see Section 19.6.8). Note that
 1452 the uncertainty of the buoyancy correction factor has been ignored here and the standard uncer-
 1453 tainty of Z has been equated with the component due to thermal expansion of the liquid, which is
 1454 assumed to be dominant. Also note that the correlation between Z and I induced by temperature
 1455 effects on both the liquid density and the balance sensitivity is unknown and has been ignored.

1456 The uncertainty of v as a predictor of the true volume that will be dispensed during a subsequent
 1457 measurement includes additional components for repeatability and temperature variability.

$$u(v) = \sqrt{Z^2 s^2(I_i) \left(1 + \frac{1}{n} \right) + v^2 \left(\varphi_{\text{Cal}}^2 + \varphi_{\text{Env}}^2 + \frac{2\beta^2 \delta T^2}{3} \right)}
 \tag{19.28}$$

1458 Note that if a different analyst performs the measurement, there may be an additional uncertainty
 1459 component associated with the difference in individual techniques.

1460 If the mean volume is within specified tolerances, a slightly simpler approach is possible. The
 1461 pipet's nominal capacity may be used as the volume v and the tolerance a may be used in a Type
 1462 B evaluation of standard uncertainty. In this case, the standard uncertainty of v is evaluated as
 1463 shown below.

$$u(v) = \sqrt{\frac{a^2}{6} + Z^2 s^2(I_i) + \frac{v^2 \beta^2 \delta T^2}{3}}
 \tag{19.29}$$

1464 The experimental procedure outlined above may also be adapted for other volume measuring
1465 devices, including flasks and graduated cylinders.

1466 The manufacturers of certain types of automatic pipetting devices (e.g., Eppendorf® pipettors)
1467 provide specifications for bias and imprecision. For these devices the manufacturer's specifica-
1468 tions for bias and imprecision may be assumed. In this case the Type B standard uncertainty of a
1469 pipetted volume v is

$$u(v) = \sqrt{\frac{a^2}{6} + s^2 + \frac{v^2 \beta^2 \delta T^2}{3}} \quad (19.30)$$

1470 where a is the manufacturer's stated bias tolerance, assumed to represent the half-width of a tri-
1471 angular distribution, and s is the stated standard deviation. This approach has the advantage of
1472 simplicity; however, since many analysts may not achieve the same accuracy as the manufac-
1473 turer, the standard uncertainty given by Equation 19.30 may be unrealistic.

1474 **19.6.10 Digital Displays and Rounding**

1475 If a measuring device, such as an analytical balance, has a digital display with resolution δ , the
1476 standard uncertainty of a measured value is at least $\delta / 2\sqrt{3}$. This uncertainty component exists
1477 even if the instrument is completely stable.

1478 A similar Type B method may be used to evaluate the standard uncertainty due to computer
1479 roundoff error. When a value x is rounded to the nearest multiple of 10^n , the component of uncer-
1480 tainty generated by roundoff error is $10^n / 2\sqrt{3}$. When rounding is performed properly and x is
1481 printed with an adequate number of figures, this component of uncertainty should be negligible
1482 in comparison to the total uncertainty of x .

1483 **EXAMPLE:** The readability of a digital balance is 0.1 mg. Therefore, the minimum standard
1484 uncertainty of a measured mass is $0.1 / 2\sqrt{3} = 0.029$ mg.

1485 **EXAMPLE:** A computer printout shows the result x of a measurement as

1486
$$3.40\text{E}+01 \pm 9.2\text{E}-02$$

1487 where the expanded uncertainty is calculated using a coverage factor of 2. The measured value
1488 is rounded to the nearest multiple of 0.1. So, the standard uncertainty of x is

1489
$$u(x) = \sqrt{\left(\frac{0.092}{2}\right)^2 + \left(\frac{0.1}{2\sqrt{3}}\right)^2} = 0.054.$$

1490 19.6.11 Subsampling

1491 Appendix F of this manual discusses laboratory subsampling. The subsampling of heterogeneous
1492 materials for laboratory analysis increases the variability of the measurement result and thus adds
1493 a component of measurement uncertainty, which is usually difficult to quantify without replicate
1494 measurements. Appendix F summarizes important aspects of the statistical theory of particulate
1495 sampling and applies the theory to subsampling in the radiation laboratory (see also Gy 1992 and
1496 Pitard 1993). The mathematical estimates obtained using the theory often require unproven
1497 assumptions about the material analyzed and rough estimates of unmeasurable parameters. How-
1498 ever, in some cases the theory can be used to suggest how subsampling errors may be affected by
1499 either changing the subsample size or grinding the material before subsampling. Of course, the
1500 total measurement uncertainty, including components contributed by subsampling, may always
1501 be evaluated by repeated subsampling and analysis.

1502 If subsampling is not repeated, its effects may be represented in the mathematical measurement
1503 model by including an input quantity F_S whose value is the ratio of the analyte concentration of
1504 the subsample to that of the total sample. This ratio, which will be called the *subsampling factor*
1505 (a MARLAP term), appears in the model as a divisor of the net instrument signal and thus is
1506 similar to the chemical yield, counting efficiency, and other sensitivity factors. The value of F_S is
1507 estimated as 1, but the value has a standard uncertainty which increases the combined standard
1508 uncertainty of the result. (Since its value is always 1, the factor F_S is an example of a “nominal
1509 value,” as discussed in Section 19.5.5.) The uncertainty of F_S also increases the MDC and the
1510 MQC.

1511 Although the component of uncertainty caused by the subsampling of heterogeneous solid matter
1512 may be difficult to estimate, it should not be ignored, since it may be relatively large and in some
1513 cases may even dominate all other components. One may use previous experience with similar

1514 materials to estimate the uncertainty, possibly with the aid of the information and methods pre-
1515 sented in Appendix F. By default, if “hot particles” are not suspected, and if reasonable precau-
1516 tions are taken to homogenize (mix) the material and to obtain a sufficient number of particles in
1517 an unbiased subsample, one may simply assume a nominal relative standard uncertainty compo-
1518 nent of 5% for solid materials.

1519 **19.6.12 The Standard Uncertainty for a Hypothetical Measurement**

1520 MARLAP’s recommended method selection criteria in Chapter 3 require that a laboratory esti-
1521 mate the standard uncertainty for the measured concentration of a hypothetical laboratory sample
1522 with a specified concentration (i.e., the “method uncertainty,” as defined by MARLAP). To
1523 estimate the combined standard uncertainty of the measured concentration, one must obtain esti-
1524 mates for all the input quantities and their standard uncertainties. All quantities except the gross
1525 instrument signal may be measured and the standard uncertainties evaluated by routine Type A
1526 and Type B methods. Alternatively, the values and their standard uncertainties may be deter-
1527 mined from historical data. The estimate of the gross signal and its standard uncertainty must be
1528 obtained by other means, since the laboratory sample is only hypothetical. The predicted value of
1529 the gross count N_S is calculated by rearranging the equation or equations in the model and solving
1530 for N_S . The standard uncertainty of the measured value may then be evaluated either from theory
1531 (e.g., Poisson counting statistics), historical data, or experimentation.

1532 **EXAMPLE:** Suppose the mathematical model for a radioactivity measurement is

1533
$$X = \frac{N_S/t_S - N_B/t_B}{M_S Y \epsilon e^{-\lambda(t_D + t_S/2)}}$$

1534 where

- 1535 X is the activity concentration (Bq kg⁻¹)
1536 N_S is the test source count
1537 N_B is the blank count
1538 t_S is the source count time (s)
1539 t_B is the blank count time (s)
1540 t_D is the decay time (s)
1541 M_S is the size of the test portion (kg)
1542 Y is the chemical yield
1543 ϵ is the counting efficiency
1544 λ is the decay constant (s⁻¹)

1545 With specified values for the concentration X , test portion size M_S , blank count N_B , count
 1546 times t_S , t_B , and t_D , efficiency ϵ , and yield Y , the source count N_S can be predicted. The pre-
 1547 dicted value is $N_S = t_S(XM_S Y \epsilon \exp(-\lambda(t_D + t_S/2)) + N_B/t_B)$. When this value is treated like a
 1548 measured value, its estimated variance according to Poisson statistics is $u^2(N_S) = N_S$. So,
 1549 assuming negligible uncertainties in the times t_S , t_B , and t_D , the uncertainty propagation for-
 1550 mula gives the combined variance of the output estimate X as

$$u_c^2(X) = \frac{u^2(N_S)/t_S^2 + u^2(N_B)/t_B^2}{M_S^2 Y^2 \epsilon^2 e^{-2\lambda(t_D + t_S/2)}} + X^2 \left(\frac{u^2(M_S)}{M_S^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(\epsilon)}{\epsilon^2} \right)$$

$$= \frac{(XM_S Y \epsilon e^{-\lambda(t_D + t_S/2)} + N_B/t_B)/t_S + N_B/t_B^2}{M_S^2 Y^2 \epsilon^2 e^{-2\lambda(t_D + t_S/2)}} + X^2 \left(\frac{u^2(M_S)}{M_S^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(\epsilon)}{\epsilon^2} \right)$$

1552 19.7 Detection and Quantification Limits

1553 19.7.1 Calculation of the Critical Value

1554 In Section 19.4.1, the *critical value* of the response variable (or gross instrument signal), denoted
 1555 by y_C , was defined as the response threshold used to decide whether the analyte concentration of
 1556 a laboratory sample is greater than that of the blank. The critical value of the net instrument
 1557 signal, denoted by S_C , was similarly defined as the net signal threshold that may be used for the
 1558 same purpose.

1559 The critical value of the net signal S_C is defined symbolically by the relation

$$\Pr[\hat{S} > S_C | X=0] = \alpha \quad (19.31)$$

1560 where $\Pr[\hat{S} > S_C | X=0]$ denotes the probability that the observed net signal \hat{S} exceeds its critical
 1561 value S_C when the true analyte concentration X is zero, and α denotes the significance level, or
 1562 the specified probability of a type I error. When the signal assumes only discrete values (e.g.,
 1563 numbers of counts), there may be no value S_C that satisfies Equation 19.31 exactly. The critical
 1564 value in this case is defined as the smallest value S_C such that $\Pr[\hat{S} > S_C | X=0] \leq \alpha$.

1565 Determining a value of S_C which satisfies the definition requires knowledge of the distribution of
1566 the net signal \hat{S} under the assumption that the analyte concentration is zero (the null hypothesis).
1567 The measured net signal may be written as $\hat{S} = \hat{Y} - \hat{B}$, where \hat{Y} denotes the measured gross
1568 signal and \hat{B} denotes the estimated value of the gross signal under the null hypothesis H_0 . In the
1569 absence of interferences, the value of \hat{B} is usually estimated by measuring one or more blanks
1570 using the same procedure used to measure the test sample, and the distribution of \hat{Y} under H_0 is
1571 determined from that of \hat{B} . In other cases, however, the value of \hat{B} includes estimated baseline
1572 and other interferences that are present only during the measurement of the sample and cannot be
1573 determined from the blank.

1574 Since S_C , not y_C , has traditionally been used for analyte detection decisions in radioanalysis, the
1575 following presentation focuses primarily on S_C . However, conversion of either of these values to
1576 the other is simple, because $y_C = S_C + \hat{B}$.

1577 19.7.1.1 Normally Distributed Signals

1578 If the distribution of the net signal \hat{S} under H_0 is approximately normal with a well-known
1579 standard deviation σ_0 , the critical value of \hat{S} is

$$S_C = z_{1-\alpha}\sigma_0 \quad (19.32)$$

1580 where $z_{1-\alpha}$ denotes the $(1 - \alpha)$ -quantile of the standard normal distribution. Table G.1 in Appen-
1581 dix G shows that $z_{1-\alpha} \approx 1.645$ when $\alpha = 0.05$. Attachment 19D describes the calculation of S_C
1582 when the standard deviation is not well-known.

1583 The blank signal \hat{B} and its standard deviation σ_B may be estimated by replicate blank measure-
1584 ments, but at least 20 measurements are generally needed to ensure that the experimental stan-
1585 dard deviation s_B is an accurate estimate of σ_B . (If fewer than 20 measurements are made, see
1586 Attachment 19D.) Given σ_B , the standard deviation σ_0 of the net signal \hat{S} under the null hypothe-
1587 sis is given equal to

$$\sigma_0 = \sigma_B \sqrt{1 + \frac{1}{n}} \quad (19.33)$$

1588 19.7.1.2 Poisson Counting

1589 Radionuclide analyses typically involve radiation counting measurements. Although radiation
 1590 counting data never follow the Poisson model exactly, the model may be a useful approximation
 1591 in some situations, especially those where the mean count is extremely low and the observed
 1592 count therefore does not follow a normal distribution. At somewhat higher count levels, features
 1593 from both models are often used, since the Poisson distribution may be approximated by a
 1594 normal distribution. In this case, the Poisson model allows one to estimate σ_0 without replication,
 1595 because one blank measurement provides an estimate of σ_B .

1596 When a test source is analyzed in a radiation counting measurement, either the gross count or the
 1597 gross count rate may be considered the instrument signal \hat{Y} . In this section, it is assumed that the
 1598 instrument signal is the gross count. Therefore,

$$\hat{Y} = N_S \qquad \hat{B} = \left(\frac{N_B}{t_B} + \hat{R}_I \right) t_S \qquad (19.34)$$

1599 and the net instrument signal is the *net count*, defined as

$$\hat{S} = N_S - \left(\frac{N_B}{t_B} + \hat{R}_I \right) t_S \qquad (19.35)$$

1600 where

1601 N_S is the gross count (source count)
 1602 N_B is the blank count
 1603 \hat{R}_I is the estimated count rate due to interferences
 1604 t_S is the count time for the test source
 1605 t_B is the count time for the blank

1606 The net signal is always assumed to have zero mean.

1607 THE POISSON-NORMAL APPROXIMATION

1608 When Poisson counting statistics are assumed (possibly with additional variance components)
 1609 and the instrument background remains stable at a level where the Poisson distribution is approx-
 1610 imately normal, the critical net count is given approximately by the equation

$$S_C = z_{1-\alpha} t_S \sqrt{\frac{R_B + R_I}{t_S} + \frac{R_B}{t_B} + \xi_B^2 + \sigma^2(\hat{R}_I)} \quad (19.36)$$

1611 where R_B denotes the (true) mean count rate of the blank, R_I denotes the mean interference count
 1612 rate, ξ_B^2 denotes non-Poisson variance in the blank (count rate) correction (see Section 19.6.4),
 1613 and $\sigma^2(\hat{R}_I)$ denotes the variance of the estimator for R_I . When there are no interferences and no
 1614 non-Poisson blank variance, this equation becomes

$$S_C = z_{1-\alpha} \sqrt{R_B t_S \left(1 + \frac{t_S}{t_B}\right)} \quad (19.37)$$

1615 The preceding formula is equivalent to “Currie’s equation” $L_C = 2.33 \sqrt{\mu_B}$ when $t_B = t_S$, $\alpha = 0.05$,
 1616 and the symbols L_C and μ_B are identified with S_C and $R_B t_S$, respectively (Currie 1968).

1617 In Equation 19.37, R_B denotes the *true* mean blank count rate, which can only be estimated. In
 1618 practice, one must substitute an estimated value \hat{R}_B for R_B , as shown in the following equation.

$$S_C = z_{1-\alpha} \sqrt{\hat{R}_B t_S \left(1 + \frac{t_S}{t_B}\right)} \quad (19.38)$$

1619 Equation 19.38 resembles Equation 19.37 (Currie’s equation) but involves the estimated count
 1620 rate \hat{R}_B , which varies with repeated measurements. The value of \hat{R}_B is usually estimated from the
 1621 same blank value N_B used to calculate the net instrument signal. (See Attachment 19D for other
 1622 possible estimators.)

$$\hat{R}_B = \frac{N_B}{t_B} \quad (19.39)$$

1623 The resulting formula, shown below, is equivalent to equations published by several authors
 1624 (Currie 1968, Lochamy 1976, Strom and Stansbury 1992, ANSI 1996a).

$$S_C = z_{1-\alpha} \sqrt{N_B \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B}\right)} \quad (19.40)$$

1625 If $\alpha = 0.05$ and $t_B = t_S$, Equation 19.40 leads to the well-known expression $2.33\sqrt{N_B}$ for the
1626 critical net count.

1627 When the blank count is high (e.g., 100 or more), Equation 19.40 works well. At lower blank
1628 levels, it can produce a high rate of type I errors. For example, if the true mean blank count is
1629 0.693, there is a 25% chance of observing 0 blank counts and a positive number of test source
1630 counts in paired measurements of equal duration. In this case, a critical value calculated by Equa-
1631 tion 19.40 produces type I errors more than 25% of the time regardless of the chosen significance
1632 level α . Attachment 19D describes several expressions for S_C that have been proposed for use in
1633 situations where the mean blank count is less than 100.

1634 **EXAMPLE**

1635 **Problem:** A 6000-s blank measurement is performed on a proportional counter and 108 beta
1636 counts are observed. A test source is to be counted for 3000 s. Estimate the critical value of the
1637 net count when $\alpha = 0.05$.

1638 **Solution:**

$$\begin{aligned}
 S_C &= z_{1-\alpha} \sqrt{N_B \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B} \right)} \\
 &= 1.645 \sqrt{108 \left(\frac{3000}{6000} \right) \left(1 + \frac{3000}{6000} \right)} \\
 &= 14.8 \text{ counts.}
 \end{aligned}$$

1640 **EXAMPLE**

1641 **Problem:** Repeat the same problem assuming the blank correction, expressed as a count rate,
1642 has a non-Poisson uncertainty component of $\xi_B = 0.001$ cps (see Section 19.6.4).

1643

Solution:

$$\begin{aligned}
 S_C &= z_{1-\alpha} \sqrt{N_B \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B}\right) + \xi_B^2 t_S^2} \\
 &= 1.645 \sqrt{108 \left(\frac{3000}{6000}\right) \left(1 + \frac{3000}{6000}\right) + (0.001)^2 (6000)^2} \\
 &= 15.6 \text{ counts.}
 \end{aligned}$$

1644

1645

So, 15.6 may be a slightly more realistic value for the critical net count.

1646

19.7.1.3 Reagent Blanks

1647

Equation 19.40 is derived with the assumption that a detection decision is based on counts obtained from a single radiation counter. When laboratory samples are analyzed in batches, it is common to analyze a single reagent blank per batch, so that the measurement conditions for the blank may differ somewhat from those of the samples. In particular, the counts for the laboratory samples and the blank may be measured using different instruments. If detection in a laboratory sample is defined relative to a reagent blank counted on a different instrument, Equation 19.40 is inappropriate. Even if a single instrument is used, the presence of positive amounts of analyte in the reagents probably invalidates the Poisson assumption. In principle, \hat{B} should be estimated by converting the total analyte activity of the reagent blank Z_{RB} to an estimated gross count on the instrument used to measure the laboratory sample. Thus,

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$$\hat{B} = F(Z_{RB}) \quad (19.41)$$

1657

where

1658

F is the calibration function for the laboratory sample measurement, whose parameters include the instrument background, counting efficiency, chemical yield, and any estimated interferences

1659

1660

1661

Z_{RB} is the estimated total activity of the reagent blank

1662

Then the net count is $\hat{S} = \hat{Y} - \hat{B}$, whose critical value is

$$S_C = z_{1-\alpha} \sqrt{\sigma^2(\hat{Y}_0) + \sigma^2(\hat{B})} \quad (19.42)$$

1663

where

1664 $\sigma^2(\hat{Y}_0)$ is the variance of the gross count \hat{Y} in the test source measurement when all of the
 1665 analyte in the source is derived from reagents

1666 $\sigma^2(\hat{B})$ is the variance of the estimator \hat{B}

1667 If Poisson counting statistics are assumed, then $\sigma^2(\hat{Y}_0)$ may be estimated by \hat{B} (assuming $\hat{B} > 0$),
 1668 but estimating $\sigma^2(\hat{B})$ still requires a more complicated expression, which may be based on uncer-
 1669 tainty propagation or replication. The variance of \hat{B} may be difficult to estimate if positive blank
 1670 values are caused not by the presence of the analyte in reagents but by contaminated glassware or
 1671 instruments, which may represent a loss of statistical control of the analytical process.

1672 19.7.2 Calculation of the Minimum Detectable Concentration

1673 The *minimum detectable concentration* (MDC) is defined as the concentration of analyte x_D that
 1674 must be present in a laboratory sample to give a probability $1 - \beta$ of obtaining a measured
 1675 response greater than its critical value, leading one to conclude correctly that the analyte concen-
 1676 tration is positive. In other words, the MDC is the analyte concentration at which the type II error
 1677 rate is β .

1678 The MDC may also be defined as the analyte concentration x_D that satisfies the relation

$$\Pr[\hat{S} \leq S_C | X = x_D] = \beta \quad (19.43)$$

1679 where the expression $\Pr[\hat{S} \leq S_C | X = x_D]$ is read as “the probability that the net signal \hat{S} does not
 1680 exceed its critical value S_C when the true concentration X is equal to x_D .”

1681 The MDC is often used as a performance measure for an analytical process for the purpose of
 1682 comparing different analytical procedures or evaluating a laboratory’s capabilities against speci-
 1683 fied requirements. The calculation of the “nominal” MDC is complicated by the fact that some
 1684 input quantities in the mathematical model, such as interferences and the chemical yield, which
 1685 have a substantial impact on the MDC, may vary significantly from measurement to measure-
 1686 ment. Other quantities that may have similar effects include the decay time, counting efficiency,
 1687 and instrument background. Because of these variable quantities, determining the value of x_D that
 1688 satisfies Equation 19.43 in practice may be difficult. The common approach to this problem is to
 1689 make conservative choices for the values of the variable quantities, which tend to increase the
 1690 value of x_D .

1691 The MDC is also commonly used in radiochemistry to describe the detection capability of the
 1692 analytical process as implemented in a particular instance. In this case, the need for conservative
 1693 choices is reduced. Instead, the measured values of the variable quantities may be used. How-
 1694 ever, since the measured values have uncertainties, their uncertainties contribute to a combined
 1695 standard uncertainty in the calculated value of x_D . For purposes of regulatory compliance, an
 1696 uncertainty interval or conservative upper bound for x_D may still be needed (see NRC 1984).

1697 19.7.2.1 The Minimum Detectable Net Instrument Signal

1698 The traditional method for calculating the MDC involves first calculating the *minimum detect-*
 1699 *able value of the net instrument signal* and then converting the result to a concentration using the
 1700 mathematical measurement model. The minimum detectable value of the net instrument signal,
 1701 denoted by S_D , is defined as the mean value of the net signal that gives a specified probability
 1702 $1 - \beta$ of yielding an observed signal greater than its critical value S_C . Thus,

$$\Pr[\hat{S} \leq S_C | S = S_D] = \beta \quad (19.44)$$

1703 where S denotes the true mean net signal.

1704 19.7.2.2 Normally Distributed Signals

1705 If the net signal \hat{S} is normally distributed and its estimated standard deviation σ_0 under H_0 is well-
 1706 known, the critical value of \hat{S} is

$$S_C = z_{1-\alpha} \sigma_0 \quad (19.45)$$

1707 as previously noted. Then, the minimum detectable net signal S_D is determined implicitly by the
 1708 equation

$$S_D = S_C + z_{1-\beta} \sqrt{\sigma^2(\hat{S} | S = S_D)} \quad (19.46)$$

1709 where $\sigma^2(\hat{S} | S = S_D)$ denotes the variance of the measured signal \hat{S} when the true mean signal S
 1710 equals S_D . If the function $\sigma^2(\hat{S} | S = S_D)$ is constant, Equation 19.46 gives the value of S_D immedi-
 1711 ately, but typically $\sigma^2(\hat{S} | S = S_D)$ is an increasing function of S_D .

1712 If the function $\sigma^2(\hat{S} | S = S_D)$ has a simple form, it may be possible to transform Equation 19.46
 1713 by algebraic manipulation into an explicit formula for S_D . For example, the variance of \hat{S} often
 1714 has the form

$$\sigma^2(\hat{S}) = aS^2 + bS + c \quad (19.47)$$

1715 where S denotes the true mean net signal and the constants a , b , and c do not depend on S (see
 1716 Section 19.7.2.3, “Poisson Counting”). In this case, the minimum detectable net signal is given
 1717 approximately by

$$S_D = \frac{1}{I_\beta} \left(S_C + \frac{z_{1-\beta}^2 b}{2} + z_{1-\beta} \sqrt{bS_C + \frac{z_{1-\beta}^2 b^2}{4} + aS_C^2 + I_\beta c} \right) \quad (19.48)$$

1718 where $I_\beta = 1 - z_{1-\beta}^2 a$.

1719 If Equation 19.46 cannot be transformed algebraically, an iterative procedure, such as fixed-point
 1720 iteration, may be used to solve the equation for S_D . An outline of fixed-point iteration is shown
 1721 below.¹¹

- 1722 1. Set $S_D = S_C + z_{1-\beta} \sqrt{\sigma^2(\hat{S} | S = S_C)}$
- 1723 2. **repeat**
- 1724 3. Set $h = S_D$
- 1725 4. Set $S_D = S_C + z_{1-\beta} \sqrt{\sigma^2(\hat{S} | S = S_D)}$
- 1726 5. **until** $|S_D - h|$ is sufficiently small
- 1727 6. **output** the solution S_D

1728 In many cases, one iteration of the loop (Lines 2–5) provides an adequate approximation of S_D . In
 1729 almost all cases, repeated iteration produces an increasing sequence of approximations

¹¹ Fixed-point iteration, or functional iteration, is the term for a general technique for solving an equation of the form $x = f(x)$. The iteration produces a sequence x_0, x_1, x_2, \dots , where $x_{n+1} = f(x_n)$. Under certain conditions, the sequence converges to a fixed point of f , where $f(x) = x$. Newton’s Method for finding a zero of a function $g(x)$ is one example of the technique.

1730 converging upward to the solution; so, the stopping condition at Line 5 may be replaced by
 1731 “until $S_D \leq h$ ” to obtain full machine precision in the result.

1732 19.7.2.3 Poisson Counting

1733 If S_C is calculated using the Poisson model and the blank is measured with a sufficiently large
 1734 number of counts, and if $\alpha = \beta$, the minimum detectable net signal S_D is given by the following
 1735 simple equation.¹²

$$S_D = z_{1-\beta}^2 + 2S_C \quad (19.49)$$

1736 In the special case when $t_S = t_B$ and $\alpha = \beta = 0.05$, Equation 19.49 becomes

$$S_D = 2.71 + 2S_C \quad (19.50)$$

1737 In the general case, S_D is determined from Equation 19.48 using the following values for a , b ,
 1738 and c .

1739
$$a = 0 \quad b = 1 \quad c = R_B t_S \left(1 + \frac{t_S}{t_B} \right)$$

1740 The resulting formula for S_D is

$$S_D = S_C + \frac{z_{1-\beta}^2}{2} + z_{1-\beta} \sqrt{\frac{z_{1-\beta}^2}{4} + S_C + R_B t_S \left(1 + \frac{t_S}{t_B} \right)} \quad (19.51)$$

1741 As previously noted, counting data never follow the Poisson model exactly. Variable factors such
 1742 as counting efficiency, and source geometry and placement tend to increase a , while interferences
 1743 and background instability tend to increase c . For example, if the counting efficiency has a 2%

¹² Some references use the value 3 instead of $z_{1-\beta}^2$ in this formula. A straightforward derivation gives the value $z_{1-\beta}^2$, which is approximately 2.71 when $\beta = 0.05$, but replacing this value by $-\ln \beta$ (approximately 3 when $\beta = 0.05$) accounts for the fact that when the mean count is low, a Poisson distribution is only imperfectly approximated by a normal distribution. The value $-\ln \beta$ is the exact value of S_D when the mean blank count rate is zero, because in this case $S_C = 0$, and $\Pr[\hat{S} = 0] \leq \beta$ if and only if $S \geq -\ln \beta$. Note also that the equation in the text is valid only if $\alpha = \beta$.

1744 coefficient of variation and background instability contributes a non-Poisson standard deviation
1745 of 0.001 cps to the blank correction, then one might use Equation 19.48 with the values

$$1746 \quad a = (0.02)^2 \quad b = 1 \quad c = R_B t_S \left(1 + \frac{t_S}{t_B} \right) + (0.001)^2 t_S^2$$

1747 19.7.2.4 The MDC

1748 Traditionally the minimum detectable net signal S_D has been converted directly to the minimum
1749 detectable concentration x_D using the same measurement model used to convert an observed
1750 value of the signal \hat{S} to a concentration \hat{x} . In a typical model, the net count is divided by the
1751 *sensitivity* A , which is the product of factors such as the count time, test portion size, counting
1752 efficiency, chemical yield, and decay factor. The sensitivity may also include the *subsampling*
1753 *factor*, denoted by F_S , which was defined in Section 19.6.11 as the ratio of the analyte concentra-
1754 tion of a subsample to that of the original sample. This factor is always estimated to be 1 and is
1755 included only for its contribution to the measurement uncertainty.

1756 If the sensitivity does not vary substantially from measurement to measurement, the MDC is
1757 given by

$$x_D = \frac{S_D}{A} \quad (19.52)$$

1758 If the variance of A is not negligible, it increases the value of x_D . Recall that when the variance of
1759 the net count \hat{S} has the form $\sigma^2(\hat{S}) = aS^2 + bS + c$, the minimum detectable net instrument signal
1760 may be approximated by Equation 19.48. If the sensitivity is normally distributed, the effect of its
1761 variance on the detection limit may be accounted for (approximately) by increasing the value of
1762 the constant a in Equation 19.48 by an amount equal to $\phi_A^2(1 + a)$, where ϕ_A denotes the relative
1763 standard deviation of A .¹³ For example, in the Poisson-counting scenario, where the value of a
1764 would otherwise be zero, a becomes ϕ_A^2 . Then the MDC is given by

¹³ The word “approximately” is used here because the signal is only approximately normal when its conditional distribution depends on the sensitivity in the manner described.

$$x_D = \frac{1}{AI_\beta} \left(S_C + \frac{z_{1-\beta}^2}{2} + z_{1-\beta} \sqrt{\frac{z_{1-\beta}^2}{4} + S_C + aS_C^2 + I_\beta R_B t_S \left(1 + \frac{t_S}{t_B} \right)} \right) \quad (19.53)$$

1765 where $I_\beta = 1 - z_{1-\beta}^2 a$ and $a = \phi_A^2$.

1766 Often the distribution of A may not be well-known or may not be approximately normal. In this
 1767 case, one may replace A in the formula by a somewhat low value, such as the β -quantile a_β of its
 1768 distribution, and ignore its variance. Thus, assuming Poisson counting statistics, one may use
 1769 Equation 19.53 with $a = 0$ and $A = a_\beta$. Alternatively, if the subsampling error is thought to be
 1770 approximately normal, one may increase a by $\phi_{\text{Samp}}^2 (1 + a)$, where ϕ_{Samp}^2 denotes the relative sub-
 1771 sampling variance, and ignore the subsampling error when estimating the quantile a_β (the
 1772 approach used in Attachment 19E). If ϕ_{Samp}^2 is negligible, the MDC may be obtained directly from
 1773 the minimum detectable net count S_D using the following formula.

$$x_D = \frac{S_D}{a_\beta} \quad (19.53)$$

1774 When a “sample-specific” MDC is calculated, the measured value of the sensitivity \hat{A} may be
 1775 substituted for A in the equation for x_D and the variance of A may be ignored. Then, if the sub-
 1776 sampling variance ϕ_{Samp}^2 is also negligible, the MDC is estimated by

$$x_D = \frac{S_D}{\hat{A}} \quad (19.54)$$

1777 However, it should be remembered that the resulting value for the MDC has an uncertainty gen-
 1778 erated by the measurement uncertainties of the input estimates from which it is calculated. It may
 1779 also be variable because of the variability of the true sensitivity factors (e.g., chemical yield).

1780 19.7.2.5 Regulatory Requirements

1781 More conservative (higher) estimates of the MDC may be obtained by following the recommen-
 1782 dations of NUREG/CR-4007, in which formulas for MDC (LLD) include estimated bounds for
 1783 relative systematic error in the blank determination (Δ_B) and the sensitivity (Δ_A). The critical net
 1784 count S_C is increased by $\Delta_B \hat{B}$, and the minimum detectable net count S_D is increased by $2 \Delta_B \hat{B}$.

1785 The MDC is then calculated by dividing S_D by the sensitivity and multiplying the result by
 1786 $1 + \Delta_A$. The approach of NUREG/CR-4007, which deals with detection limits, differs fundamen-
 1787 tally from that of the *GUM*, which considers only measurement uncertainty. The NUREG's
 1788 conservative approach treats random errors and systematic errors differently to ensure that the
 1789 MDC for a measurement process is unlikely to be consistently underestimated, which is an
 1790 important consideration if the laboratory is required by regulation or contract to achieve a speci-
 1791 fied MDC.

1792 19.7.2.6 Testing the MDC

1793 To ensure that the MDC has been estimated properly, one may test the estimate experimentally
 1794 by analyzing n identical control samples spiked with an analyte concentration equal to x_D . If the
 1795 MDC has been determined properly (the null hypothesis), the probability of failing to detect the
 1796 analyte in each control sample is at most β . Then the number of nondetectable results in the
 1797 experiment may be assumed to have a binomial distribution with parameters n and β . If k non-
 1798 detectable results are actually obtained, one calculates the cumulative binomial probability

$$P = \sum_{j=k}^n \binom{n}{j} \beta^j (1 - \beta)^{n-j} \quad \text{or} \quad 1 - \sum_{j=0}^{k-1} \binom{n}{j} \beta^j (1 - \beta)^{n-j} \quad (19.55)$$

1799 and rejects the null hypothesis if P is smaller than the chosen significance level for the test
 1800 (which may differ from the significance level for the analyte detection test).

1801 To make the test realistic, one should ensure that the physical and chemical characteristics of the
 1802 control samples, including potential interferences, are representative of laboratory samples
 1803 encountered in practice.

1804

EXAMPLE

1805 **Problem:** Assume x_D is estimated with $\beta = 0.05$. As a check, 10 control samples spiked with
 1806 concentration x_D are analyzed and 3 of the 10 produce nondetectable results. Does x_D appear to
 1807 have been underestimated (at the 2% level of significance)?

1808 **Solution:** The variables are $n = 10$, $\beta = 0.05$, and $k = 3$. Calculate the P -value

1809
$$P = 1 - \sum_{j=0}^2 \binom{10}{j} (0.05)^j (0.95)^{10-j} = 1 - 0.9885 = 0.0115$$

1810 Since $P \leq 0.02$, reject the null hypothesis and conclude that the MDC was underestimated.

1811 **19.7.3 Calculation of the Minimum Quantifiable Concentration**

1812 The *minimum quantifiable concentration* (MQC), or the *minimum quantifiable value* of the con-
 1813 centration, was defined in Section 19.4.5 as the analyte concentration in a laboratory sample that
 1814 gives measured results with a specified relative standard deviation $1 / k_Q$, where k_Q is usually
 1815 chosen to be 10.

1816 Calculation of the MQC requires that one be able to estimate the standard deviation for the result
 1817 of a hypothetical measurement performed on a laboratory sample with a specified analyte con-
 1818 centration. Section 19.6.12 discusses the procedure for calculating the standard deviation for such
 1819 a hypothetical measurement.

1820 The MQC is defined symbolically as the value x_Q that satisfies the relation

$$x_Q = k_Q \sqrt{\sigma^2(\hat{X} | X = x_Q)} \tag{19.56}$$

1821 where $\sigma^2(\hat{X} | X = x_Q)$ denotes the variance of the estimator \hat{X} when the true concentration X
 1822 equals x_Q . If the function $\sigma^2(\hat{X} | X = x_Q)$ has a simple form, it may be possible to solve Equation
 1823 19.56 for x_Q using only algebraic manipulation. Otherwise, fixed-point iteration, which was
 1824 introduced in Section 19.7.2, may be used. The use of fixed-point iteration for this purpose is
 1825 shown below.

- 1826 1. Set $x_Q = k_Q \sqrt{\sigma^2(\hat{X} | X = 0)}$
 1827 2. **repeat**
 1828 3. Set $h = x_Q$

- 1829 4. Set $x_Q = k_Q \sqrt{\sigma^2(\hat{X} | X = x_Q)}$
 1830 5. **until** $|x_Q - h|$ is sufficiently small
 1831 6. **output** the solution x_Q

1832 The sequence of values generated by the algorithm typically converges upward to the solution.

1833 When Poisson counting statistics are assumed, possibly with excess variance components, and
 1834 the mathematical model for the analyte concentration is $X = S / AF_S$, where S is the net count, A
 1835 denotes the overall sensitivity of the measurement, and F_S is the subsampling factor, Equation
 1836 19.56 may be solved for x_Q to obtain the formula

$$x_Q = \frac{k_Q^2}{2AI_Q} \left(1 + \sqrt{1 + \frac{4I_Q}{k_Q^2} \left(R_B t_S \left(1 + \frac{t_S}{t_B} \right) + \xi_B^2 t_S^2 + R_I t_S + \sigma^2(\hat{R}_I) t_S^2 \right)} \right) \quad (19.57)$$

1837 where

- 1838 t_S is the count time for the test source
 1839 t_B is the count time for the blank
 1840 R_B is the mean blank count rate
 1841 ξ_B^2 is the non-Poisson variance component of the blank count rate correction
 1842 R_I is the mean interference count rate
 1843 $\sigma(\hat{R}_I)$ is the standard deviation of the measured interference count rate
 1844 $\phi_{\hat{A}}^2$ is the relative variance of the measured sensitivity, \hat{A}
 1845 ϕ_{Samp}^2 is the relative subsampling variance
 1846 I_Q is equal to $1 - k_Q^2 (\phi_{\hat{A}}^2 + \phi_{\text{Samp}}^2)$

1847 If the true sensitivity A may vary, then a conservative value, such as the 0.05-quantile $a_{0.05}$,
 1848 should be substituted for A in the formula. Note that $\phi_{\hat{A}}^2$ denotes only the relative variance of \hat{A}
 1849 due to measurement error — it does not include the variance of the true sensitivity, A .

1850 Note that Equation 19.57 defines the MQC only if $I_Q > 0$. If $I_Q \leq 0$, the MQC is defined to be
 1851 infinite, because there is no concentration at which the relative standard deviation of \hat{X} fails to
 1852 exceed $1 / k_Q$. In particular, if the relative standard deviation of the measured sensitivity \hat{A} or the
 1853 subsampling standard deviation ϕ_{Samp} exceeds $1 / k_Q$, then $I_Q < 0$ and the MQC is infinite.

1854 More generally, if the variance of the measured concentration \hat{X} can be expressed in the form
1855 $\sigma^2(\hat{X}) = aX^2 + bX + c$, where a , b , and c do not depend on X , then the MQC is given by the
1856 formula

$$x_Q = \frac{k_Q^2}{2(1 - k_Q^2 a)} \left(b + \sqrt{b^2 + \frac{4c(1 - k_Q^2 a)}{k_Q^2}} \right) \quad (19.58)$$

1857 For example, if pure Poisson counting statistics are assumed and there are no interferences, then
1858 $a = \phi_A^2 + \phi_{\text{Samp}}^2$, $b = 1 / A$, and $c = R_B t_S (1 + t_S / t_B) / A^2$.

1859 19.8 References

1860 This section contains a combined list of references for Chapter 19 and its attachments.

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ATTACHMENT 19A

Distributions

1982
1983

1984 19A.1 Introduction

1985 This attachment briefly describes the probability distributions used in Chapter 19.

1986 Distributions may be classified according to their mathematical properties. Distributions in the
1987 same class or family are described by the same mathematical formulas. The formulas involve
1988 numerical parameters which distinguish one member of the class from another.

1989 Two important kinds of distributions are the normal and log-normal, which are observed often in
1990 nature. Other types of distributions important in radioanalysis include the rectangular, binomial,
1991 Poisson, Student's t , chi-square, and exponential distributions. Poisson distributions in particular
1992 are important in radiation counting measurements and are described in Section 19.6.2.

1993 19A.2 Normal Distributions

1994 Many quantities encountered in nature and in the laboratory have distributions which can be
1995 described by the "bell curve." This type of distribution, called a *normal*, or *Gaussian*, distribu-
1996 tion, is usually a reasonably good model for the result of a radioanalytical measurement. A num-
1997 ber of commonly used methods for evaluating data sets depend on their having an approximately
1998 normal distribution. The probability density function (pdf) for a normal distribution is shown in
1999 Figure 19.5.

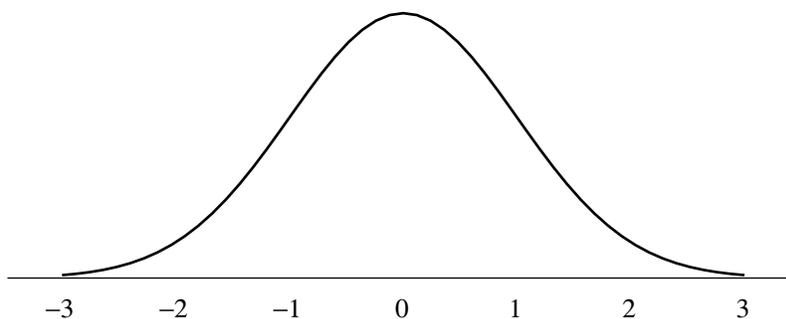


FIGURE 19.5 — A normal distribution

2000 A normal distribution is uniquely specified by its mean μ and variance σ^2 . The normal distribu-
2001 tion with mean 0 and variance 1 is called the *standard normal distribution*. If X is normally dis-
2002 tributed with mean μ and variance σ^2 , then $(X - \mu) / \sigma$ has the standard normal distribution.

2003 The sum of a large number of independent random variables has an approximately normal distri-
2004 bution, even if the individual variables themselves are not normally distributed, so long as the
2005 variance of each term is much smaller than the variance of the sum.¹⁴ This is one reason why the
2006 normal distribution occurs often in nature. When a quantity is the result of additive processes
2007 involving many small random variations, the quantity tends to be normally distributed. It is also
2008 true that many other distributions, such as the binomial, Poisson, Student's *t*, and chi-square, can
2009 be approximated by normal distributions under certain conditions.

2010 The mean value of a normal distribution is also its mode, or most likely value, which corresponds
2011 to the location of the peak of the curve shown in Figure 19.5. Since the distribution is symmetric
2012 about this point, the mean is also the median, or the value that splits the range into equally likely
2013 portions.

2014 The value of a normally distributed quantity will be within one standard deviation of the mean
2015 about 68% of the time. It will be within two standard deviations about 95% of the time and
2016 within three standard deviations more than 99% of the time. It is important to remember that
2017 these percentages apply only to normal distributions.

2018 19A.3 Log-normal Distributions

2019 The concentration of a contaminant in the environment may not be normally distributed. Instead
2020 it often tends to be *log-normally* distributed, as shown in Figure 19.6.

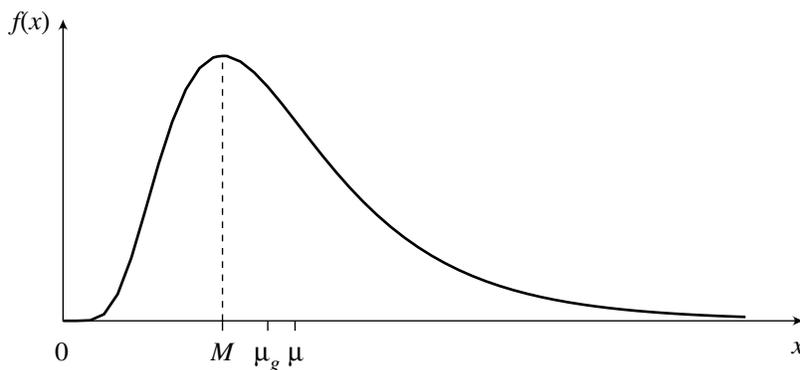


FIGURE 19.6 — A log-normal distribution

¹⁴ The number of quantities required to obtain a sum that is approximately normal depends on the distribution of the quantities. If the distribution is already 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.

2021 By definition, a quantity X has a log-normal distribution if the logarithm of X is normally distrib-
 2022 uted. The product of a large number of independent positive random variables with similar var-
 2023 iances is approximately log-normal, because the logarithm of the product is a sum of independent
 2024 random variables, and the sum is approximately normal. The concentration of a contaminant in
 2025 the environment tends to be log-normal because it is the result of processes of concentration and
 2026 dilution, which are multiplicative.

2027 The distribution of a log-normal quantity X can be uniquely specified by the mean $\mu_{\ln X}$ and
 2028 variance $\sigma_{\ln X}^2$ of $\ln X$, but more commonly used descriptors are the *geometric mean* $\mu_g =$
 2029 $\exp(\mu_{\ln X})$ and the *geometric standard deviation* $\sigma_g = \exp(\sigma_{\ln X})$. The geometric mean and geomet-
 2030 ric standard deviation are defined so that, if k is a positive number, the probability that X will fall
 2031 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,
 2032 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
 2033 μ_g / σ_g^2 and $\mu_g \sigma_g^2$ about 95% of the time.

2034 Although the mean, median, and mode of a normal distribution are identical, for a log-normal
 2035 distribution these three values are distinct. The median, in fact, is the same as the geometric
 2036 mean μ_g . As shown in Figure 19.6, the mean μ is larger than the geometric mean μ_g and the mode
 2037 M is smaller. The mean and mode may be calculated from the geometric mean and geometric
 2038 standard deviation as shown in Table G.6 in Appendix G.¹⁵

2039 The log-normal distribution is important for the interpretation of environmental radiation data,
 2040 but it may also have applications in the laboratory. Two possible applications are decay factors
 2041 $e^{-\lambda t}$ based on uncertain time measurements and concentrations of contaminants in laboratory
 2042 reagents.

2043 **19A.4 Chi-square Distributions**

2044 If Z_1, Z_2, \dots, Z_v are independent random variables and each has the standard normal distribution,
 2045 the sum $Z_1^2 + Z_2^2 + \dots + Z_v^2$ has a *chi-square* (or *chi-squared*) *distribution with v degrees of free-*
 2046 *dom*. A chi-square distribution, like a log-normal distribution, is asymmetric and does not include
 2047 negative values. For large v the chi-square distribution is approximately normal. Figure 19.7
 2048 shows the densities for chi-square distributions with 1, 2, 3, and 10 degrees of freedom.

¹⁵ Given the mean μ and standard deviation σ , the geometric mean and geometric standard deviation may be calculated as $\mu_g = \mu^2 / \sqrt{\mu^2 + \sigma^2}$ and $\sigma_g = \exp(\sqrt{\ln(1 + \sigma^2 / \mu^2)})$.

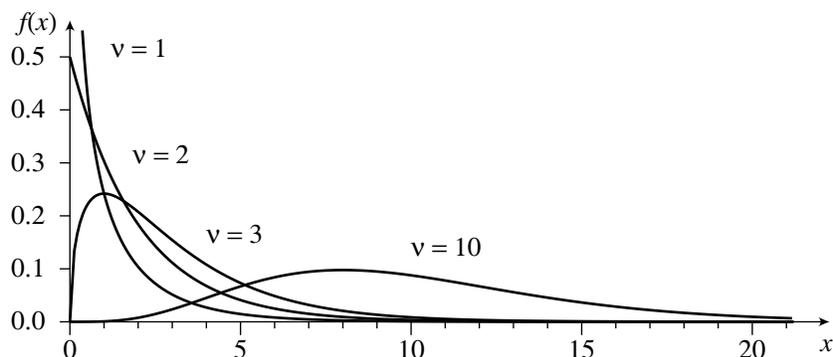


FIGURE 19.7 — Chi-square distributions

2049 Chi-square distributions are used frequently in hypothesis testing, especially for tests of hypothe-
 2050 ses about the variances of normally distributed data. Chi-square distributions also appear in least-
 2051 squares analysis (see Attachment 19B).

2052 A sum of independent chi-square random variables is also chi-square. Specifically, if X and Y are
 2053 independent chi-square random variables with v_1 and v_2 degrees of freedom, respectively, then
 2054 $X + Y$ has a chi-square distribution with $v_1 + v_2$ degrees of freedom.

2055 The mean of a chi-square distribution equals the number of degrees of freedom v , and the vari-
 2056 ance equals $2v$. The mode equals zero if $v \leq 2$ and equals $v - 2$ otherwise. The median does not
 2057 have a simple formula.

2058 **19A.5 T-Distributions**

2059 If Z is standard normal, X is chi-square with v degrees of freedom, and Z and X are independent,
 2060 then $Z / \sqrt{X/v}$ has a *Student's t-distribution with v degrees of freedom*. A t -distribution is sym-
 2061 metric and mound-shaped like a normal distribution and includes both positive and negative
 2062 values. Figure 19.8 shows the pdf for a t -distribution with 3 degrees of freedom. A dotted stan-
 2063 dard normal curve is also shown for comparison.

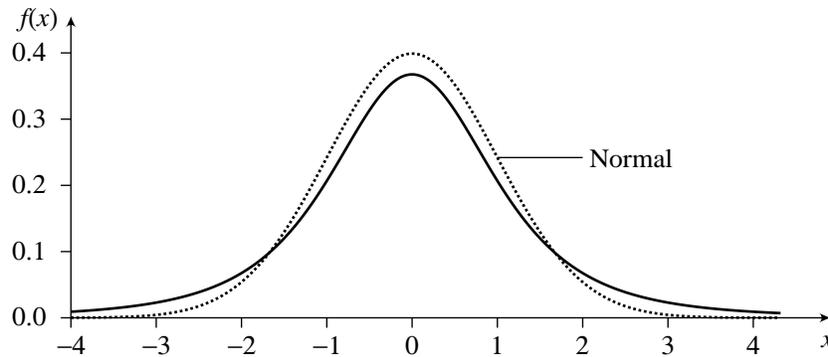


FIGURE 19.8 — The t -distribution with 3 degrees of freedom

2064 When v is large, the t -distribution is virtually identical to the standard normal distribution.

2065 The median and mode of a t -distribution are both zero. The mean is also zero if $v > 1$ but is
 2066 undefined for $v = 1$. The variance equals $v / (v - 2)$ if $v > 2$ and is undefined otherwise.

2067 T -distributions are often used in tests of hypotheses about the means of normally distributed data
 2068 and are important in statistical quality control. T -distributions are also used in the procedure
 2069 described in Attachment 19C for calculating measurement coverage factors.

2070 If X_1, X_2, \dots, X_n are independent and normally distributed with the same mean μ and the same
 2071 variance, then the quantity

$$\frac{\bar{X} - \mu}{s_x / \sqrt{n}}$$

2072 where \bar{X} is the arithmetic mean and s_x is the experimental standard deviation, has a t -distribution
 2073 with $n - 1$ degrees of freedom.

2074 If X_1, X_2, \dots, X_n, Y are independent and normally distributed with the same mean and variance,
 2075 then the quantity

$$\frac{Y - \bar{X}}{s_x \sqrt{1 + 1/n}}$$

2076 where \bar{X} is the arithmetic mean of the X_i and s_X is the experimental standard deviation, has a t -
2077 distribution with $n - 1$ degrees of freedom.

2078 If Z is standard normal, X is chi-square with v degrees of freedom, Z and X are independent, and
2079 δ is a constant, then $(Z + \delta) / \sqrt{X/v}$ has the *non-central t -distribution* with v degrees of freedom
2080 and non-centrality parameter δ . When the (central) t -distribution is used to test the null hypothe-
2081 sis that two normal distributions have the same mean, a non-central t -distribution describes the
2082 distribution of the test statistic if the null hypothesis is false. For example, if X_1, X_2, \dots, X_n, Y are
2083 independent and normally distributed with the same variance σ^2 , and X_1, X_2, \dots, X_n have the same
2084 mean μ_X , then the statistic

2085
$$\frac{Y - \bar{X}}{s_X \sqrt{1 + 1/n}}$$

2086 where \bar{X} is the arithmetic mean of the X_i and s_X is the experimental standard deviation, has a t -
2087 distribution with $n - 1$ degrees of freedom if $\mu_X = \mu_Y$, but it has a non-central t -distribution with
2088 non-centrality parameter

2089
$$\delta = \frac{\mu_Y - \mu_X}{\sigma \sqrt{1 + 1/n}}$$

2090 if $\mu_X \neq \mu_Y$.

2091 The non-central t -distribution is useful in the theory of detection limits and appears in Section
2092 19D.3.2 of Attachment 19D.

2093 **19A.6 Rectangular Distributions**

2094 If X only assumes values between a_- and a_+ and all such values are equally likely, the distribution
2095 of X is called a *rectangular distribution*, or a *uniform distribution* (see Figure 19.9).

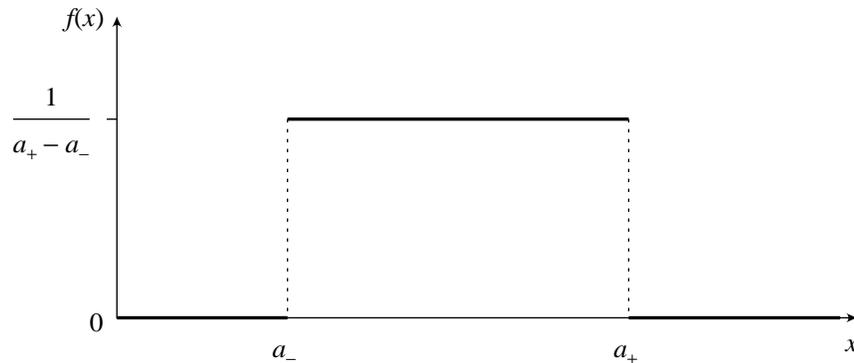


FIGURE 19.9 — A rectangular distribution

2096 The mean and median of the rectangular distribution equal the midrange $(a_- + a_+) / 2$, and the
 2097 standard deviation is $(a_+ - a_-) / 2\sqrt{3}$. The rectangular distribution is multimodal.

2098 Rectangular distributions are frequently used for Type B evaluations of standard uncertainty (see
 2099 Sections 19.5.2.2 and 19.6.10).

2100 **19A.7 Trapezoidal and Triangular Distributions**

2101 Another type of bounded distribution used for Type B evaluations of standard uncertainty is a
 2102 *trapezoidal* distribution, which is described in Section 19.5.2.2. If X has a trapezoidal distribu-
 2103 tion, it only assumes values between two numbers a_- and a_+ , but values near the midrange
 2104 $(a_- + a_+) / 2$ are more likely than those near the extremes. The pdf for a symmetric trapezoidal
 2105 distribution is shown in Figure 19.10. Asymmetric trapezoidal distributions are not considered
 2106 here.

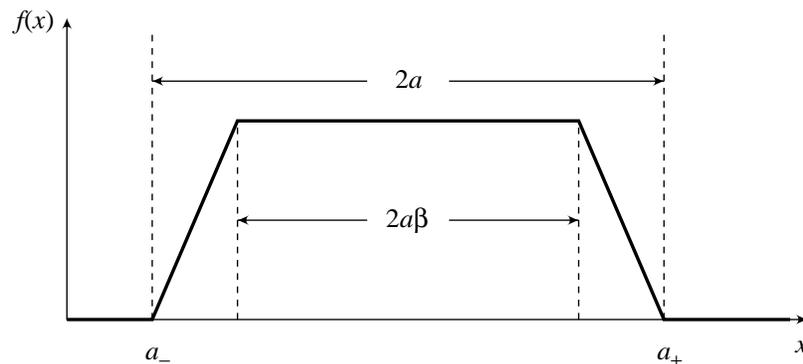


FIGURE 19.10 — A trapezoidal distribution

2107 The mean and median of this distribution are both equal to the midrange. If the width of the trap-
 2108 ezoid at its base is $2a$ and the width at the top is $2a\beta$, where $0 < \beta < 1$, then the standard deviation
 2109 is $a\sqrt{(1 + \beta^2) / 6}$. As β approaches 0, the trapezoidal distribution approaches a *triangular distri-*
 2110 *bution*, whose standard deviation is $a / \sqrt{6}$, or $(a_+ - a_-) / 2\sqrt{6}$. As β approaches 1, the distribution
 2111 approaches the rectangular distribution described in Section 19A.6.

2112 **19A.8 Exponential Distributions**

2113 The *exponential distribution* describes the life of an unstable atomic nucleus, whose remaining
 2114 life does not depend on its current age. The distribution is described by one parameter, often
 2115 denoted by λ , which represents the fractional decay rate. The mean of the distribution is $1 / \lambda$ and
 2116 its variance is $1 / \lambda^2$. The mode is zero, and the median is the same as the half-life of the radio-
 2117 nuclide. The pdf for an exponential distribution is shown in Figure 19.11.

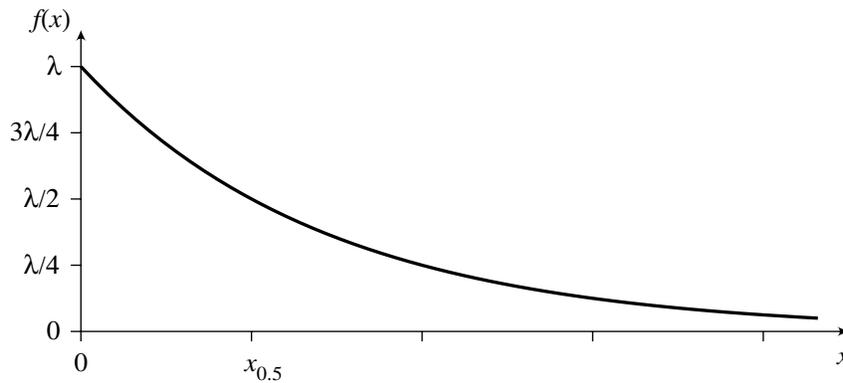


FIGURE 19.11 — An exponential distribution

2118 The exponential distribution also describes waiting times between events in a Poisson process.
 2119 For example, if the instrument background for a radiation counter follows the Poisson model
 2120 with mean count rate R_B , the waiting times between counts are exponentially distributed with
 2121 parameter R_B .

2122 **19A.9 Binomial Distributions**

2123 The *binomial distribution*, introduced in Section 19.6.2, arises when one counts the outcomes of
 2124 a series of n independent and identical experiments, each of which can produce the result
 2125 “success” or “failure.” If the probability of success for each event is p , the number of successes
 2126 has a binomial distribution with parameters n and p . Important facts about the binomial distribu-
 2127 tion include the following:

- 2128 • The distribution is discrete; its only possible values are 0, 1, 2, ..., n .
- 2129 • The mean of the distribution is np .
- 2130 • The variance is $np(1 - p)$.
- 2131 • If n is large and p is not close to 0 or 1, the distribution is well approximated by a normal
- 2132 distribution.

2133 If X is binomial with parameters n and p , then for $k = 0, 1, 2, \dots, n$, the probability that $X = k$ is
 2134 given by the equation

$$\Pr[X = k] = \binom{n}{k} p^k (1 - p)^{n-k} \quad (19.61)$$

2135 **19A.10 Poisson Distributions**

2136 As explained in Section 19.6.2, the *Poisson distribution* arises naturally as an approximation to
 2137 the binomial distribution when n is large and p is small. Even if n is not large, the variance of the
 2138 binomial distribution can be approximated using the Poisson model if p is small. Other important
 2139 facts about a Poisson distribution include the following:

- 2140 • The distribution is discrete; its only possible values are the nonnegative integers
- 2141 0, 1, 2,
- 2142 • The mean and variance of the distribution are equal.
- 2143 • If the mean is large, the distribution is well approximated by a normal distribution.
- 2144 • A sum of independent Poisson random variables is also Poisson.

2145 If X has a Poisson distribution with mean μ , then for any nonnegative integer n , the probability
 2146 that $X = n$ is given by

$$\Pr[X = n] = e^{-\mu} \frac{\mu^n}{n!} \quad (19.62)$$

2147 The Poisson distribution is related to the chi-square distribution, since

TABLE 19.3 — 95% confidence interval for a Poisson mean

n	$\mu_{\text{lower}} = \frac{1}{2}\chi_{0.025}^2(2n)$	$\mu_{\text{upper}} = \frac{1}{2}\chi_{0.975}^2(2n + 2)$
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

$$\Pr[X \leq n] = \Pr[\chi^2(2n + 2) \geq 2\mu] \quad \text{and} \quad \Pr[X \geq n] = \Pr[\chi^2(2n) \leq 2\mu] \quad (19.63)$$

2148 where $\chi^2(v)$ denotes a chi-square random variable with v degrees of freedom. This fact allows one
 2149 to use quantiles of a chi-square distribution to construct a confidence interval for μ based on a
 2150 single observation $X = n$. Table 19.3 lists 95% two-sided confidence intervals for μ some small
 2151 values of n . For larger values of n , the quantiles $\chi_p^2(2n)$ and $\chi_p^2(2n + 2)$ may be approximated
 2152 using the Wilson-Hilferty formula (NBS 1964):

$$\chi_p^2(v) \approx v \left(1 - \frac{2}{9v} + z_p \sqrt{\frac{2}{9v}} \right)^3 \quad (19.64)$$

2153 As noted above, when the mean μ is large, the Poisson distribution may be approximated by a
 2154 normal distribution. Specifically,

$$\Pr[X \leq n] \approx \Phi \left(\frac{n + 0.5 - \mu}{\sqrt{\mu}} \right) \quad (19.65)$$

2155 where Φ denotes the distribution function of the standard normal distribution. For most purposes,
 2156 this approximation is adequate if $\mu \geq 20$.

2157 **19A.11 References**

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2160 **ATTACHMENT 19B**
2161 **Multicomponent Analyses**

2162 **19B.1 Matrix Equations**

2163 A multicomponent mathematical model may require the simultaneous solution of a system of
2164 equations formulated in terms of vector and matrix operations, which are implemented in soft-
2165 ware. For example, one procedure for radiostromtium analysis involves the precipitation of stron-
2166 tium from a sample, followed by multiple beta measurements of the precipitate over a period of
2167 time. Both ⁸⁹Sr and ⁹⁰Sr are beta emitters, and ⁹⁰Sr decays to ⁹⁰Y, another beta emitter. The half-
2168 life of ⁹⁰Y is short enough (64 h) that significant ingrowth occurs over a period of several days,
2169 allowing the activities of ⁸⁹Sr and ⁹⁰Sr to be determined from the changing count rate.

2170 The net beta count y_i for a measurement of duration t_i at time Δt_i after precipitation has an
2171 expected value given by

$$a_{i1}x_1 + a_{i2}x_2 = E(y_i) \quad (19.66)$$

2172 where

2173 x_1 is the ⁸⁹Sr activity in the precipitate
2174 x_2 is the ⁹⁰Sr activity in the precipitate
2175 a_{i1} is a function of t_i , Δt_i , and the ⁸⁹Sr counting efficiency and half-life
2176 a_{i2} is a function of t_i , Δt_i , and the ⁹⁰Sr and ⁹⁰Y counting efficiencies and half-lives

2177 If m measurements are performed, Equation 19.66 is repeated for each measurement, giving a
2178 system of m equations. After replacing $E(y_i)$ by the measured value y_i , one can rewrite the
2179 equations as approximations in the form

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 &\approx y_1 \\ a_{21}x_1 + a_{22}x_2 &\approx y_2 \\ &\vdots \\ a_{m1}x_1 + a_{m2}x_2 &\approx y_m \end{aligned} \quad (19.67)$$

2180 or in matrix form as $\mathbf{Ax} \approx \mathbf{y}$. If $m \geq 2$, the system of equations can be solved simultaneously for x_1
2181 and x_2 . If there are exactly two measurements ($m = 2$), the system can be solved easily without
2182 matrix operations, but if additional measurements are made ($m > 2$), a least-squares solution,

2183 which typically involves matrix algebra, is required. The use of matrix algebra can make uncer-
2184 tainty propagation more tedious.

2185 **19B.2 Random Vectors and Matrices**

2186 Uncertainty propagation in matrix equations is best described in terms of random vectors and
2187 random matrices. A useful exposition of matrix theory in this manual is impractical; so, some
2188 familiarity with the basic concepts must be assumed. These basic concepts will be extended to
2189 incorporate randomness.

2190 A *random vector* is a vector whose components are random variables. Similarly, a *random*
2191 *matrix* is a matrix whose components are random variables.

2192 Vectors are usually denoted by bold lower-case letters and matrices by bold upper-case letters.
2193 The i^{th} component of a vector \mathbf{v} is denoted by v_i . The ij^{th} component of a matrix \mathbf{A} is usually
2194 denoted by a_{ij} . The transpose of a matrix \mathbf{A} will be denoted here by \mathbf{A}' . If \mathbf{A} is square and
2195 invertible, the inverse is denoted by \mathbf{A}^{-1} . The length of a vector \mathbf{v} is denoted by $\|\mathbf{v}\|$.

2196 The *expected value* of a random vector \mathbf{x} is defined as the vector $E(\mathbf{x})$ whose i^{th} component
2197 is $E(x_i)$. The expected value of a random matrix \mathbf{Y} is similarly defined as the matrix $E(\mathbf{Y})$ whose
2198 ij^{th} component is $E(y_{ij})$. The *covariance matrix* of a column vector \mathbf{x} and a column vector \mathbf{y} is
2199 defined by

$$\text{Cov}(\mathbf{x}, \mathbf{y}) = E[(\mathbf{x} - E(\mathbf{x}))(\mathbf{y} - E(\mathbf{y}))'] \quad (19.68)$$

2200 The *covariance matrix* of a random column vector \mathbf{x} (or the *variance-covariance matrix*) is
2201 defined by

$$V(\mathbf{x}) = \text{Cov}(\mathbf{x}, \mathbf{x}) \quad (19.69)$$

2202 The covariance matrix gets its name from the fact that the ij^{th} component of $\text{Cov}(\mathbf{x}, \mathbf{y})$ equals the
2203 covariance $\text{Cov}(x_i, y_j)$.¹⁶ When \mathbf{x} and \mathbf{y} are vectors of measured values, the estimated covariance
2204 matrices will be denoted here by $\mathbf{u}(\mathbf{x}, \mathbf{y})$ and $\mathbf{u}^2(\mathbf{x})$.

¹⁶ In the literature, one often sees the covariance matrix for \mathbf{x} and \mathbf{y} denoted by Σ_{xy} , and the variance-covariance matrix for \mathbf{x} denoted by Σ_x .

2205 **19B.3 Linear Least Squares**

2206 Assume y_1, y_2, \dots, y_m are independent, normally distributed measured results and $V(y_i) = \sigma_i^2$ for
 2207 each i . Let x_1, x_2, \dots, x_n denote unknown quantities on which the y_i depend and whose values one
 2208 needs to determine. Assume the means $E(y_i)$ are related to the quantities x_j by the following
 2209 system of equations.

$$\begin{aligned}
 a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n &= E(y_1) \\
 a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n &= E(y_2) \\
 &\vdots \\
 a_{m1}x_1 + a_{m2}x_2 + \cdots + a_{mn}x_n &= E(y_m)
 \end{aligned}
 \tag{19.70}$$

2210 For example the y_i might be measured beta counts of a sample and the x_j could represent the
 2211 unknown activities of ^{89}Sr and ^{90}Sr in the sample at the time of collection.

2212 The linear system 19.70 can be represented using matrix notation as

$$\mathbf{Ax} = E(\mathbf{y}) \tag{19.71}$$

2213 Typically $E(\mathbf{y})$ is unknown and must be replaced in Equation 19.71 by the measured vector \mathbf{y} , but
 2214 there may be no vector \mathbf{x} for which \mathbf{Ax} exactly equals \mathbf{y} . So, it is necessary to find an approximate
 2215 solution $\hat{\mathbf{x}}$ such that $\mathbf{A}\hat{\mathbf{x}}$ is close to \mathbf{y} in some sense. The components of the difference $\mathbf{A}\hat{\mathbf{x}} - \mathbf{y}$ are
 2216 called *residuals*, and when $\mathbf{A}\hat{\mathbf{x}}$ is close to \mathbf{y} , the residuals should be small. If $\sigma_i = 1$ for all i , the
 2217 method of *least squares* finds a vector $\hat{\mathbf{x}}$ that minimizes the sum of the squares of the residuals
 2218 $\text{SSRES} = \|\mathbf{A}\hat{\mathbf{x}} - \mathbf{y}\|^2$. If $\sigma \neq 1$ for some i , then both sides of equation i should be divided by σ_i
 2219 before applying the least-squares method. So, if \mathbf{W} denotes the $m \times m$ diagonal matrix whose i^{th}
 2220 diagonal element is $1 / \sigma_i^2$, then $\text{SSRES} = (\mathbf{A}\hat{\mathbf{x}} - \mathbf{y})' \mathbf{W} (\mathbf{A}\hat{\mathbf{x}} - \mathbf{y})$. In practice, the standard devia-
 2221 tions σ_i are usually replaced by the standard uncertainties $u(y_i)$.

2222 A least-squares solution always exists. If $\text{rank } \mathbf{A} < n$, there may be more than one solution, but
 2223 this case only occurs if the measurement process is inadequate even in principle for determining
 2224 the unknown quantities. So, in practice $\text{rank } \mathbf{A} = n$. (The *rank* of \mathbf{A} is the number of linearly

2225 independent columns or rows.) Under this assumption the unique least-squares solution is given
 2226 by Equation 19.72.¹⁷

$$\hat{\mathbf{x}} = (\mathbf{A}'\mathbf{W}\mathbf{A})^{-1}\mathbf{A}'\mathbf{W}\mathbf{y} \quad (19.72)$$

2227 When quantities such as the test portion size V and chemical yield Y can be factored out of the
 2228 matrix \mathbf{A} , it is generally better to do so. The presence of such variables increases the variance of
 2229 the least-squares solution $\hat{\mathbf{x}}$, making critical values unnecessarily large when they are calculated
 2230 as described in Section 19B.6. When quantities such as V and Y are factored out, the components
 2231 of the least-squares solution $\hat{\mathbf{x}}$ must be divided by the missing factors to obtain activity concen-
 2232 trations, and the uncertainties in the factors must be propagated.

2233 Approximating the standard deviations σ_i in the weight matrix \mathbf{W} by the standard uncertainties
 2234 $u(y_i)$ may bias the least-squares solution slightly if y_i and $u(y_i)$ are correlated, which happens, for
 2235 example, when y_i is a measured count and $u(y_i)$ is the Poisson counting uncertainty calculated
 2236 from a single measurement. This bias can be virtually eliminated by using the initial least-squares
 2237 solution to refine the values of the standard uncertainties and then repeating the least-squares
 2238 procedure using the refined estimates.

2239 The solution $\hat{\mathbf{x}}$ is a random vector, because it is a function of the random vector \mathbf{y} . The covariance
 2240 matrix for $\hat{\mathbf{x}}$ is

$$\mathbf{u}^2(\hat{\mathbf{x}}) = (\mathbf{A}'\mathbf{W}\mathbf{A})^{-1} \quad (19.73)$$

2241 The diagonal elements of this matrix are the variances of the components of $\hat{\mathbf{x}}$, and the off-
 2242 diagonal elements are the covariances. This expression for the covariance matrix is complete
 2243 only when there are no uncertainties in the coefficient matrix \mathbf{A} . A more general formula for the
 2244 covariance matrix is presented in Section 19B.5.

2245 In some cases, the variance of each y_i may be unknown, although all components of \mathbf{y} are
 2246 believed to have the same variance. When this is true, the solution $\hat{\mathbf{x}}$ may be computed by

$$\hat{\mathbf{x}} = (\mathbf{A}'\mathbf{A})^{-1}\mathbf{A}'\mathbf{y} \quad (19.74)$$

¹⁷ For some least-squares problems, a direct calculation of the solution $\hat{\mathbf{x}}$ using Equation 19.72 can be computationally unstable. *Singular value decomposition* of the matrix \mathbf{A} gives a more stable method for obtaining $\hat{\mathbf{x}}$ but is beyond the scope of this document. The SVD method also allows one to find a least-squares solution (not unique) when $\text{rank } \mathbf{A} < n$. See Lawson 1974 or Press et al. 1992 for more details.

2247 and the variance of the components y_i may be estimated by

$$u^2(y_i) = \frac{\|A\hat{\mathbf{x}} - \mathbf{y}\|^2}{m - n} \quad (19.75)$$

2248 (The use of Equation 19.75 is a Type A evaluation of uncertainty with $m - n$ degrees of
2249 freedom.) When this equation is used, the covariance matrix for $\hat{\mathbf{x}}$ is

$$\mathbf{u}^2(\hat{\mathbf{x}}) = u^2(y_i)(A'A)^{-1} \quad (19.76)$$

2250 **19B.4 General Least Squares**

2251 The general least-squares problem arises when there is a set of measured values y_1, y_2, \dots, y_m ,
2252 whose expected values are functions of an n -dimensional vector \mathbf{x} of unknown quantities, as
2253 indicated by the following system of equations.

$$\begin{aligned} f_1(\mathbf{x}) &= E(y_1) \\ f_2(\mathbf{x}) &= E(y_2) \\ &\vdots \\ f_m(\mathbf{x}) &= E(y_m) \end{aligned} \quad (19.77)$$

2254 The system of equations can be written in matrix form as $\mathbf{f}(\mathbf{x}) = E(\mathbf{y})$ The method of least squares
2255 finds a vector $\hat{\mathbf{x}}$ that minimizes the sum of the squares of the residuals

$$\text{SSRES} = \sum_{i=1}^m \left(\frac{f_i(\hat{\mathbf{x}}) - y_i}{u(y_i)} \right)^2 = (\mathbf{f}(\hat{\mathbf{x}}) - \mathbf{y})' \mathbf{W} (\mathbf{f}(\hat{\mathbf{x}}) - \mathbf{y}) \quad (19.78)$$

2256 When $\mathbf{f}(\hat{\mathbf{x}})$ can be written as $A\hat{\mathbf{x}}$ for some matrix A , the problem is linear least squares, whose
2257 solution was presented in the preceding section. When the functions f_i are nonlinear but differen-
2258 tiable, the solution can be obtained by iterative approximation methods. The most commonly
2259 used algorithm for nonlinear least squares is the Levenberg-Marquardt algorithm (Press et al.
2260 1992). Whatever algorithm is used, it should compute the covariance matrix $\mathbf{u}^2(\hat{\mathbf{x}})$, described in
2261 the next section. For more details on nonlinear least-squares problems, see Marquardt 1963,
2262 Press et al. 1992, or Bevington 1992.

2263 **19B.5 The Covariance Matrix for a Least-Squares Solution**

2264 Let $A = \partial f / \partial x$ denote the $m \times n$ matrix whose ij^{th} component is $\partial f_i / \partial x_j$.¹⁸ Then the covariance
2265 matrix for the least-squares solution \hat{x} is approximately equal to $(A'WA)^{-1}$.

2266 It often happens that the function f depends on variables other than x , whose values, like the
2267 components of y , are measured before the least-squares method is applied. In the strontium
2268 analysis described at the beginning of this attachment, the measured counting efficiencies for
2269 ^{89}Sr , ^{90}Sr , and ^{90}Y are good examples. Measurement uncertainties in these variables contribute to
2270 the uncertainties in the solution \hat{x} , although the least-squares covariance matrix $(A'WA)^{-1}$
2271 accounts only for uncertainties in the measurement of y . Better estimates of the variances and
2272 covariances of the components of \hat{x} require that the expression for the covariance matrix be
2273 expanded.

2274 Let the additional measured quantities be written as a vector z with components z_1, z_2, \dots, z_r , and
2275 write $f(x; z)$ to indicate that f depends on both x and z . Assume the components of z are measured
2276 independently of y , and the covariance matrix $u^2(z)$ is known. If the method of least squares is
2277 applied to find the unique solution \hat{x} that minimizes SSRES, and if the uncertainties in the com-
2278 ponents z_i are small, the covariance matrix for the solution is

$$u^2(\hat{x}) = (A'WA)^{-1} + \left(\frac{\partial \hat{x}}{\partial z} \right) u^2(z) \left(\frac{\partial \hat{x}}{\partial z} \right)' \quad (19.79)$$

2279 where $\partial \hat{x} / \partial z$ denotes the $n \times r$ matrix whose ij^{th} component is $\partial \hat{x}_i / \partial z_j$. The j^{th} column of $\partial \hat{x} / \partial z$
2280 may be calculated using the formula

$$\frac{\partial \hat{x}}{\partial z_j} = (A'WA)^{-1} \left(\frac{\partial A'}{\partial z_j} W(y - f(\hat{x}; z)) - A'W \frac{\partial f}{\partial z_j} \right) \quad (19.80)$$

2281 If the uncertainties in the components z_i are not small, another method of solution may be needed
2282 (e.g., see Fuller 1987).

2283 When the least-squares problem is linear, the j^{th} column of $\partial f / \partial z$ is given by the formula

¹⁸ The matrix A is the *Jacobian* matrix of the component functions f_1, f_2, \dots, f_m .

$$\frac{\partial \mathbf{f}}{\partial z_j} = \frac{\partial \mathbf{A}}{\partial z_j} \hat{\mathbf{x}} \quad (19.81)$$

2284 and the ij^{th} component is given by

$$\frac{\partial f_i}{\partial z_j} = \sum_{k=1}^n \frac{\partial a_{ik}}{\partial z_j} \hat{x}_k \quad (19.82)$$

2285 When the problem is nonlinear, the components $\partial f_i / \partial z_j$ are calculated by other means.

2286 19B.6 Critical Values

2287 The general approach to the determination of critical values even in the case of nonlinear least
 2288 squares is conceptually no different from that outlined in Section 19.7.1. The standard uncer-
 2289 tainty of a signal or response variable is determined under the null hypothesis H_0 and then multi-
 2290 plied by an appropriate factor, such as the normal quantile $z_{1-\alpha}$. The response variable for a
 2291 component x_j may be taken to be the corresponding component \hat{x}_j of the least-squares solution
 2292 vector. Let \mathbf{x}^* denote the value of the vector \mathbf{x} under H_0 . It will be assumed here that $x_j^* = 0$, but
 2293 note that the null hypothesis must give values not only to x_j but to all the components of \mathbf{x} ,
 2294 because the value of one component generally affects the measurement uncertainties of the other
 2295 components of the solution vector. Generally, for this purpose one must use the measured values
 2296 of all the components of \mathbf{x} except x_j , although these values may not be known accurately.

2297 To determine the critical value, first calculate the vector $\mathbf{y}^* = \mathbf{f}(\mathbf{x}^*)$, which is the expected value of
 2298 \mathbf{y} under H_0 . If the least-squares problem is linear, then $\mathbf{y}^* = \mathbf{A}\mathbf{x}^*$. Next calculate the diagonal
 2299 weight matrix \mathbf{W} , whose i^{th} diagonal element is the inverse $1 / u^2(y_i)$ of the estimated variance of
 2300 y_i under the null hypothesis. For example, if the problem is the strontium problem described in
 2301 Section 19B.1, in which y_i denotes a net count, then $u^2(y_i)$ might be the counting variance given
 2302 by

$$u^2(y_i) = a_{i1}x_1^* + a_{i2}x_2^* + R_{B,i}t_i \left(1 + \frac{t_i}{t_{B,i}} \right) \quad (19.83)$$

2303 where $R_{B,i}$ is the blank count rate and $t_{B,i}$ is the corresponding count time. Finally, evaluate the
 2304 covariance matrix \mathbf{C} for the solution of the least-squares problem $\mathbf{f}(\hat{\mathbf{x}}) \cong \mathbf{y}^*$, as described in

2305 Section 19B.5. (The solution vector $\hat{\mathbf{x}}$ here equals \mathbf{x}^* because of the method by which \mathbf{y}^* was
2306 constructed.) Then the critical value of the j^{th} component \hat{x}_j is $z_{1-\alpha}\sqrt{c_{jj}}$, where $z_{1-\alpha}$ is the
2307 $(1 - \alpha)$ -quantile of the standard normal distribution.

2308 **19B.7 Detection and Quantification Limits**

2309 Computing the minimum detectable value of a component x_j requires one to find the value d such
2310 that $d = z_{1-\alpha}\sqrt{V(0)} + z_{1-\beta}\sqrt{V(d)}$, where $V(x_j)$ denotes the variance of the estimator \hat{x}_j as a func-
2311 tion of the true value x_j . The value of $V(x_j)$ is the j^{th} diagonal element of the covariance matrix \mathbf{C}
2312 determined under the assumption that the true value of the j^{th} component is x_j . Solving for d pre-
2313 cisely generally requires an iterative algorithm, which generates a sequence of values converging
2314 to d . Given that $V(x_j)$ and its derivative can be calculated, the equation may be solved by Newton-
2315 Raphson iteration. A simpler version of fixed-point iteration, which does not involve the deriv-
2316 ative, may also be used. The use of fixed-point iteration for this purpose is described in Section
2317 19.7.

2318 The problem of determining the minimum quantifiable value of a concentration estimated by the
2319 least-squares methods is similar to that of finding the minimum detectable value and generally
2320 requires an iterative algorithm (e.g., see Section 19.7).

2321 **19B.8 References**

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ATTACHMENT 19C Estimation of Coverage Factors

2333

19C.1 Introduction

2334 Although it is common for laboratories to use a fixed coverage factor such as 2 or 3 when deter-
2335 mining an expanded uncertainty for a measured value, the true coverage probability for the resul-
2336 ting interval may be lower than expected if the standard uncertainties of the input estimates are
2337 determined from evaluations with too few degrees of freedom. This attachment summarizes a
2338 general method presented in Annex G of the *GUM* for determining appropriate coverage factors
2339 in these circumstances (ISO 1995). Section 19C.3 applies the method to Poisson counting
2340 uncertainties.

2341

19C.2 Procedure

2342 Assume the mathematical model for a measurement is $Y = f(X_1, X_2, \dots, X_N)$, the input estimates
2343 x_1, x_2, \dots, x_N are independent, and the output estimate is $y = f(x_1, x_2, \dots, x_N)$. Also assume that the
2344 combined standard uncertainty of y is not dominated by one component determined from a Type
2345 A evaluation with only a few degrees of freedom or from a Type B evaluation based on a distri-
2346 bution very different from a normal distribution. Then the distribution of the output estimate y
2347 should be approximately normal, and the following procedure may be used to obtain a coverage
2348 factor k_p for the expanded uncertainty of y that gives a desired coverage probability p .

2349 First compute the *effective degrees of freedom* ν_{eff} of the measurement using the *Welch-*
2350 *Satterthwaite* formula

$$\nu_{\text{eff}} = \frac{u_c^4(y)}{\sum_{i=1}^N \frac{u_i^4(y)}{\nu_i}} \quad (19.84)$$

2351 Here $u_i(y) = |\partial y / \partial x_i| u(x_i)$ is the component of the combined standard uncertainty generated by
2352 $u(x_i)$. If $u(x_i)$ is evaluated by a Type A method, then ν_i is the number of degrees of freedom for
2353 that evaluation. If $u(x_i)$ is evaluated instead by a Type B method, then ν_i is defined to be

$$\nu_i = \frac{1}{2} \frac{u^2(x_i)}{\sigma^2[u(x_i)]} = \frac{1}{2} \left(\frac{\Delta u(x_i)}{u(x_i)} \right)^{-2} \quad (19.85)$$

2354 where $\Delta u(x_i)$ is the estimated standard deviation of the standard uncertainty $u(x_i)$. Estimation of
 2355 $\Delta u(x_i)$ often requires professional judgment.

2356 In some cases, one may consider the value of $\Delta u(x_i)$ for a Type B standard uncertainty to be zero
 2357 or negligible, as for example when evaluating the uncertainty associated with rounding a number
 2358 (Section 19.6.10). In such cases, one may assume $v_i = \infty$; so, the i^{th} term of the sum appearing in
 2359 the denominator of the Welch-Satterthwaite formula vanishes.

2360 The coverage factor k_p is defined to be the $(1 + p) / 2$ -quantile $t_{(1+p)/2}(v_{\text{eff}})$ of a t -distribution with
 2361 v_{eff} degrees of freedom.¹⁹ Since the calculated value of v_{eff} will generally not be an integer, it must
 2362 be truncated to an integer, or else an interpolated t -factor should be used. That is, if
 2363 $n < v_{\text{eff}} < n + 1$, then use either $k_p = t_{(1+p)/2}(v_{\text{eff}})$ or

$$k_p = (n + 1 - v_{\text{eff}})t_{(1+p)/2}(n) + (v_{\text{eff}} - n)t_{(1+p)/2}(n + 1) \quad (19.86)$$

2364 The expanded uncertainty $U_p = k_p u_c(y)$ is estimated to have a coverage probability approximately
 2365 equal to p .

2366 19C.3 Poisson Counting Uncertainty

2367 As stated in Section 19.5.2.2, the standard uncertainty in the number of counts n observed during
 2368 a radiation measurement may often be estimated by $u(n) = \sqrt{n}$, according to the Poisson counting
 2369 model. This method of evaluating the standard uncertainty is a Type B method; so, the effective
 2370 degrees of freedom v for the evaluation should be determined from $\Delta u(n)$. The standard deviation
 2371 of \sqrt{n} is always less than 0.65.²⁰ If n is greater than about 10, the standard deviation of \sqrt{n} is

¹⁹ The *GUM* uses the notation $t_p(v)$ to denote the $(1 + p) / 2$ -quantile of a t -distribution with v 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.

²⁰ 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 $f(\lambda)$ whose value is the variance of the square root of a Poisson random variable with mean λ . The first derivative of f is positive, decreasing, and convex between $\lambda = 0$ and the location of the maximum of the function at $\lambda = 1.31895$; so, Newton's Method converges to the solution from below. The maximum value of f is found to be $(0.642256)^2$.

2372 approximately equal to 0.5, and, in this case, Equation 19.85 gives the estimate $v \approx 2n$. For
 2373 smaller values of n , the same approximation is inadequate.

2374 MARLAP recommends that the standard uncertainty $u(n)$ and degrees of freedom v for a Poisson
 2375 measured value n be estimated by

$$u(n) = \sqrt{n} \quad \text{and} \quad v = 2n \quad (19.87)$$

2376 or, if very low counts are possible, by

$$u(n) = \sqrt{n + 1} \quad \text{and} \quad v = 2(n + 1) \quad (19.88)$$

2377 If the expected count is greater than about 10, these formulas tend to give a coverage probability
 2378 near the desired probability p . When the expected count is small, the coverage probability tends
 2379 to be greater than p .

2380 Although the estimate $u(n) = \sqrt{n + 1}$ may be derived by the Bayesian approach to counting statis-
 2381 tics assuming a flat prior distribution for the mean count (Friedlander et al. 1981), the recom-
 2382 mended expressions for $u(n)$ and v in Equation 19.88 have been chosen for the purely practical
 2383 reason that they are simple and seem to give satisfactory results. When the count is low, the
 2384 assumptions underlying the Welch-Satterthwaite formula are usually violated, because the com-
 2385 bined standard uncertainty is dominated by counting uncertainty, and the distribution of the count
 2386 is not normal. However, even in this case, if the formula is used, the recommended expressions
 2387 for $u(n)$ and v tend to give conservative results.

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ATTACHMENT 19D Low-Background Detection Limits

2400 **19D.1 Overview**

2401 This attachment describes methods for determining critical values and minimum detectable con-
2402 centrations (MDCs) when the standard deviation of the blank signal is not known precisely,
2403 which occurs for example when the blank is measured by low-background Poisson counting or
2404 when the standard deviation is estimated from a small number of replicate measurements.

2405 **19D.2 Calculation of the Critical Value**

2406 The critical value of the net signal S_C was defined earlier by the relation

$$\Pr[\hat{S} > S_C | X = 0] = \alpha \quad (19.89)$$

2407 When the signal assumes only discrete values (e.g., numbers of counts), there may be no value S_C
2408 that satisfies Equation 19.89 exactly. The critical value in this case is defined as the smallest
2409 value S_C such that $\Pr[\hat{S} > S_C | X = 0] \leq \alpha$.

2410 19D.2.1 Normally Distributed Signals

2411 If the distribution of the net signal \hat{S} under H_0 is approximately normal with a well-known stan-
2412 dard deviation, σ_0 , the critical value of \hat{S} is

$$S_C = z_{1-\alpha} \sigma_0 \quad (19.90)$$

2413 where $z_{1-\alpha}$ denotes the $(1 - \alpha)$ -quantile of the standard normal distribution. Typically the stan-
2414 dard deviation σ_0 is not well-known and must therefore be replaced by an estimate, $\hat{\sigma}_0$. If $\hat{\sigma}_0$ is
2415 determined by a statistical evaluation with ν degrees of freedom, the multiplier $z_{1-\alpha}$ should be
2416 replaced by $t_{1-\alpha}(\nu)$, the $(1 - \alpha)$ -quantile of the t -distribution with ν degrees of freedom (cf. Type
2417 A evaluation of standard uncertainty in Section 19.5.2.1). Thus,

$$S_C = t_{1-\alpha}(\nu) \hat{\sigma}_0 \quad (19.91)$$

2418 Table G.2 in Appendix G lists values of $t_{1-\alpha}(v)$. In general, $t_{1-\alpha}(v)$ is greater than $z_{1-\alpha}$, but the two
 2419 values are approximately equal if v is large.

2420 When \hat{B} is estimated by the average of n replicate blank measurements (assuming no interfer-
 2421 ences), the standard deviation $\hat{\sigma}_0$ of the net signal \hat{S} under the null hypothesis may be estimated
 2422 from the experimental standard deviation of the measured blank values, s_B . Specifically,

$$\hat{\sigma}_0 = s_B \sqrt{1 + \frac{1}{n}} \quad (19.92)$$

2423 The number of degrees of freedom, v , in this case equals $n - 1$; so, the critical value of \hat{S} is

$$S_C = t_{1-\alpha}(n - 1) s_B \sqrt{1 + \frac{1}{n}} \quad (19.93)$$

2424 19D.2.2 Poisson Counting

2425 It is assumed here, as in Section 19.7, that the instrument is a radiation counter and the instru-
 2426 ment signal is the gross count. Therefore,

$$\hat{Y} = N_S \quad \hat{B} = \left(\frac{N_B}{t_B} + \hat{R}_I \right) t_S \quad (19.94)$$

2427 and the net instrument signal is the *net count*, defined as

$$\hat{S} = N_S - \left(\frac{N_B}{t_B} + \hat{R}_I \right) t_S \quad (19.95)$$

2428 where

- 2429 N_S is the gross count (source count)
- 2430 N_B is the blank count
- 2431 \hat{R}_I is the estimated count rate due to interferences
- 2432 t_S is the count time for the test source
- 2433 t_B is the count time for the blank

2434 If the mean blank count rate, R_B , is well-known and there are no interferences, then according to
 2435 the Poisson model, the critical gross count, y_C , equals the smallest nonnegative integer n such that

$$e^{-R_B t_S} \sum_{k=0}^n \frac{(R_B t_S)^k}{k!} \geq 1 - \alpha \tag{19.96}$$

2436 Then S_C , the critical net count, equals $y_C - N_B t_S / t_B$. Table 19.4 shows critical gross counts for
 2437 $\alpha = 0.05$ for small values of $R_B t_S$ (adapted from NRC 1984).²¹ To use the table, one calculates the
 2438 value of $R_B t_S$, finds the appropriate line in the table, and compares the observed gross count N_S to
 2439 the value of y_C read from the table. The analyte is considered detected if and only if $N_S > y_C$.
 2440 When $R_B t_S$ is greater than about 20, y_C may be approximated by

$$y_C = \lfloor 0.5 + R_B t_S + z_{1-\alpha} \sqrt{R_B t_S} \rfloor \tag{19.97}$$

2441 where $z_{1-\alpha}$ denotes the $(1 - \alpha)$ -quantile of the standard normal distribution, and $\lfloor x \rfloor$ denotes the
 2442 largest integer not greater than x .

TABLE 19.4 — Critical gross count (well-known blank)

$R_B t_S$	y_C	$R_B t_S$	y_C	$R_B t_S$	y_C
0.000–0.051	0	5.425–6.169	10	13.255–14.072	20
0.051–0.355	1	6.169–6.924	11	14.072–14.894	21
0.355–0.818	2	6.924–7.690	12	14.894–15.719	22
0.818–1.366	3	7.690–8.464	13	15.719–16.549	23
1.366–1.970	4	8.464–9.246	14	16.549–17.382	24
1.970–2.613	5	9.246–10.036	15	17.382–18.219	25
2.613–3.285	6	10.036–10.832	16	18.219–19.058	26
3.285–3.981	7	10.832–11.634	17	19.058–19.901	27
3.981–4.695	8	11.634–12.442	18	19.901–20.746	28
4.695–5.425	9	12.442–13.255	19	20.746–21.594	29

²¹ The breaks in the table occur at $R_B t_S = 0.5 \chi_{0.05}^2(2y_C)$ and $0.5 \chi_{0.05}^2(2y_C + 2)$.

2443 When the blank count rate R_B is low, which is often true for alpha counting, measuring its value
 2444 with good relative precision tends to be difficult, especially if the instrument background tends to
 2445 drift. However, a conservative bound, such as a $1 - \alpha$ upper confidence limit, may be used if one
 2446 wishes to limit type I error rates and is willing to tolerate the resulting higher detection limits.
 2447 More commonly used methods for calculating the critical value are described below.

2448 THE POISSON-NORMAL APPROXIMATION

2449 As stated in Section 19.7.1.2, when Poisson counting statistics are assumed (possibly with
 2450 additional variance components) and the instrument background remains stable between meas-
 2451 urements at a level where the Poisson distribution is approximately normal, the critical net count
 2452 is given approximately by the equation

$$S_C = z_{1-\alpha} t_S \sqrt{\frac{R_B + R_I}{t_S} + \frac{R_B}{t_B} + \xi_B^2 + \sigma^2(\hat{R}_I)} \quad (19.98)$$

2453 where R_B denotes the (true) mean count rate of the blank, R_I denotes the mean interference count
 2454 rate, ξ_B^2 denotes non-Poisson variance in the blank (count rate) correction, and $\sigma^2(\hat{R}_I)$ denotes the
 2455 variance of the estimator for R_I . When there are no interferences and no non-Poisson blank
 2456 variance, this equation becomes

$$S_C = z_{1-\alpha} \sqrt{R_B t_S \left(1 + \frac{t_S}{t_B} \right)} \quad (19.99)$$

2457 Low mean blank levels cause the Poisson distribution to deviate from the normal model. Figure
 2458 19.12 shows the effects of these deviations on the type I error rates for the Poisson-normal
 2459 approximation when $t_B = t_S$ and $\alpha = 0.05$. The graph has discontinuities because of the discrete
 2460 nature of the Poisson distribution, but the type I error rate is approximately correct (equal to 0.05)
 2461 when the mean blank count is 10 or more.²²

²² Probabilities on the curve are calculated using the equation

$$P(\mu) = 1 - e^{-2\mu} \sum_{n=0}^{\infty} \frac{\mu^n}{n!} \sum_{k=0}^{\lfloor n+2.33\sqrt{\mu} \rfloor} \frac{\mu^k}{k!}$$

where μ denotes the (true) mean blank count. Terms of the infinite sum are accumulated until the cumulative Poisson probability, $e^{-\mu} \sum_{i=0}^n \mu^i / i!$, approaches 1. The calculated values agree with those listed in Table 1 of

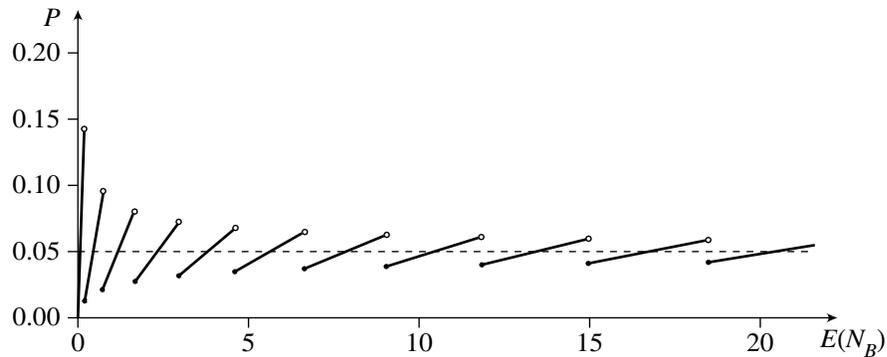


FIGURE 19.12 — Type I error rate for the Poisson-normal approximation ($t_B = t_S$)

2462 In Equation 19.99, R_B denotes the *true* mean blank count rate, which can only be estimated. In
 2463 practice, one must substitute an estimated value, \hat{R}_B , as shown in the following equation.

$$S_C = z_{1-\alpha} \sqrt{\hat{R}_B t_S \left(1 + \frac{t_S}{t_B} \right)} \quad (19.100)$$

2464 The most frequently used expressions for S_C may be derived from Equation 19.100 using an
 2465 estimator \hat{R}_B that equals a weighted average of the measured blank count rate N_B / t_B and the
 2466 measured source count rate N_S / t_S . A weighted average of both measured rates may be used here
 2467 to estimate the true blank level for the purpose of the hypothesis test, because, under the null
 2468 hypothesis of zero net source activity, both measured rates are unbiased estimates of the true
 2469 blank count rate. Given nonnegative weights w_S and w_B such that $w_S + w_B = 1$, the mean blank
 2470 count rate is estimated by

$$\hat{R}_B = w_S \frac{N_S}{t_S} + w_B \frac{N_B}{t_B} \quad (19.101)$$

Brodsky 1992. The discontinuities occur at $\mu = k^2 / 2.33^2$ for $k = 1, 2, 3, \dots$

2471 This estimate \hat{R}_B is always unbiased under the null hypothesis of zero net activity and no inter-
 2472 ferences, but the choice of weights affects the variance of the estimator. (When interferences are
 2473 present, this weighted average is inappropriate.)²³

2474 This attachment will use the notation \tilde{S}_C , which is nonstandard, to denote any version of the
 2475 critical value that depends on the gross signal N_S (or \hat{Y}).

2476 It is often convenient to eliminate N_S from the expression for \tilde{S}_C (e.g., when calculating the
 2477 MDC). When the same measured value of N_B is used to calculate both the critical value \tilde{S}_C and
 2478 the net signal \hat{S} , elimination of N_S from Equation 19.100 produces the following formula for an
 2479 alternative critical value S_C .²⁴

$$S_C = \frac{z_{1-\alpha}^2 w_S}{2} \left(1 + \frac{t_S}{t_B} \right) + z_{1-\alpha} \sqrt{\frac{z_{1-\alpha}^2 w_S^2}{4} \left(1 + \frac{t_S}{t_B} \right)^2 + N_B \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B} \right)} \quad (19.102)$$

2480 It is not generally true that $S_C = \tilde{S}_C$ unless $w_S = 0$, but either critical value may be used to imple-
 2481 ment the same test for analyte detection, because $\hat{S} > S_C$ if and only if $\hat{S} > \tilde{S}_C$.

2482 If there is additional non-Poisson variance associated with the blank correction, an extra term
 2483 may be included under the radical (e.g., $\xi_B^2 t_S^2$, where ξ_B^2 is as in Equation 19.98), although at very
 2484 low background levels the Poisson variance tends to dominate this excess component.

2485 FORMULA A

2486 The most commonly used approach for calculating S_C is given by Formula A (shown below).

²³ The common practice of using the same Poisson measurement data to calculate both the net signal \hat{S} and its critical value tends to produce a correlation between the two variables. This correlation does not exist when the critical value is determined by a statistical evaluation of normally distributed data as described earlier in the attachment.

²⁴ The critical value \tilde{S}_C may be written as a function $f(\hat{S})$ of the observed net signal \hat{S} and the blank count N_B . Then \hat{S} exceeds \tilde{S}_C if and only if it exceeds the fixed point of f , which is the value S_C where $f(S_C) = S_C$. The fixed point is a function of N_B but not of N_S .

$$S_C = z_{1-\alpha} \sqrt{N_B \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B} \right)} \tag{19.103}$$

Formula A

2487 If $\alpha = 0.05$ and $t_B = t_S$, Formula A leads to the well-known expression $2.33\sqrt{N_B}$ for the critical net
 2488 count (e.g., see Currie 1968).

2489 Formula A may be derived from the standard approximation by using the blank measurement
 2490 alone to estimate the true blank count rate — i.e., by using the weights $w_S = 0$ and $w_B = 1$.

2491 As noted in Section 19.7.1.2, when the blank count is high (e.g., 100 or more), Formula A works
 2492 well, but at lower blank levels, it can produce a high rate of type I errors. Figure 19.13 shows
 2493 type I error rates for Formula A as a function of the mean blank count for count time ratios
 2494 $t_B / t_S = 1$ and 5 when $\alpha = 0.05$.²⁵

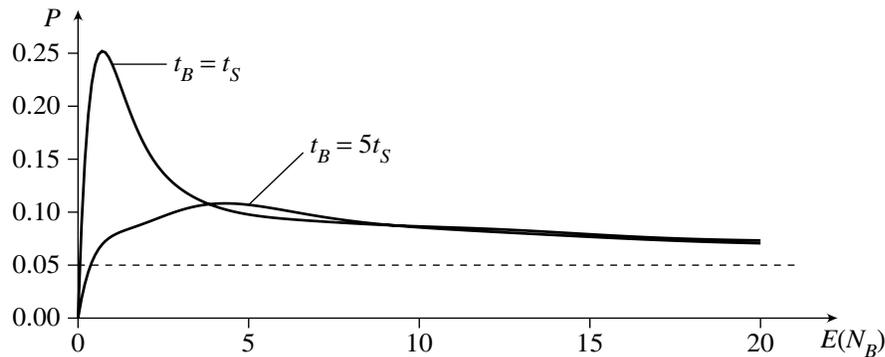


FIGURE 19.13 — Type I error rates for Formula A

²⁵ Probabilities on the two curves are calculated using the equation

$$P(\mu) = 1 - e^{-\mu(1+t_S/t_B)} \sum_{n=0}^{\infty} \frac{\mu^n}{n!} \frac{[y_C(n)]}{\sum_{k=0}^{[y_C(n)]} \frac{(\mu t_S/t_B)^k}{k!}}$$

where $y_C(n) = n(t_S/t_B) + 1.645\sqrt{n(t_S/t_B)(1+t_S/t_B)}$ and μ denotes the mean blank count. The same equation with different expressions for $y_C(n)$ is used to calculate the type I error rates shown in Figures 19.14–17.

2495 FORMULA B

2496 Another published formula for the critical value is (equivalent to) the following (Nicholson
2497 1966).

$$\tilde{S}_C = z_{1-\alpha} \sqrt{N_S + N_B \frac{t_S^2}{t_B^2}} \quad (19.104)$$

2498 The critical value calculated by Equation 19.104 equals $z_{1-\alpha}$ times the combined standard uncer-
2499 tainty of the net count. This fact is the basis for the original derivation of the formula, but the
2500 formula may also be derived from Equation 19.100 using the weights $w_S = t_B / (t_S + t_B)$ and $w_B =$
2501 $t_S / (t_S + t_B)$ to estimate \hat{R}_B . When N_S is eliminated from Equation 19.104, one obtains Formula B
2502 (below), which is equivalent to the equation for the critical value given in *Atoms, Radiation, and*
2503 *Radiation Protection* (Turner 1995).

$$S_C = \frac{z_{1-\alpha}^2}{2} + z_{1-\alpha} \sqrt{\frac{z_{1-\alpha}^2}{4} + N_B \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B}\right)} \quad (19.105)$$

Formula B

2504 Type I error rates for Formula B are shown in Figure 19.14.

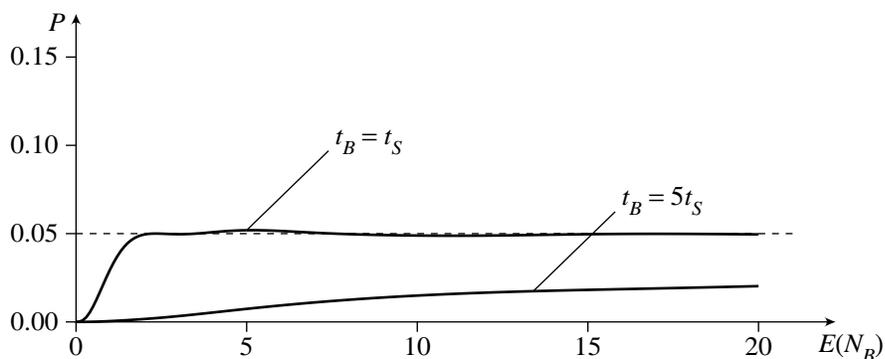


FIGURE 19.14 — Type I error rates for Formula B

2505 Formula B appears natural and intuitive when it is derived in terms of the combined standard
 2506 uncertainty of the net count, and it gives excellent results when $t_B = t_S$ and the pure Poisson
 2507 model is valid. However, when the formula is derived using the weights w_S and w_B , as described
 2508 above, the expression seems much less natural, because the weights clearly are not optimal when
 2509 $t_B \neq t_S$. Notice that when $t_B > t_S$, the type I error rate tends to be less than α .

2510 **FORMULA C**

2511 If the pure Poisson model is valid, then under the null hypothesis, the weights $w_S = t_S / (t_S + t_B)$
 2512 and $w_B = t_B / (t_S + t_B)$ provide the minimum-variance unbiased estimator \hat{R}_B for the mean blank
 2513 count rate and lead to the following formula for the critical net count (Nicholson 1963, 1966).²⁶

$$\tilde{S}_C = z_{1-\alpha} \sqrt{(N_S + N_B) \frac{t_S}{t_B}} \quad (19.106)$$

2514 Elimination of N_S from Equation 19.106 produces Formula C, shown below.

$$S_C = \frac{z_{1-\alpha}^2 t_S}{2t_B} + z_{1-\alpha} \sqrt{\frac{z_{1-\alpha}^2 t_S^2}{4t_B^2} + N_B \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B}\right)} \quad (19.107)$$

Formula C

2515 Formula C is equivalent to the equation for the “decision threshold” given in Table 1 of ISO
 2516 11929-1 (ISO 2000a) for the case of fixed-time counting. Figure 19.15 shows type I error rates
 2517 for Formula C.

²⁶ The approach here is conceptually similar to that of a two-sample t -test, which employs a pooled estimate of variance in the comparison of two normal populations.

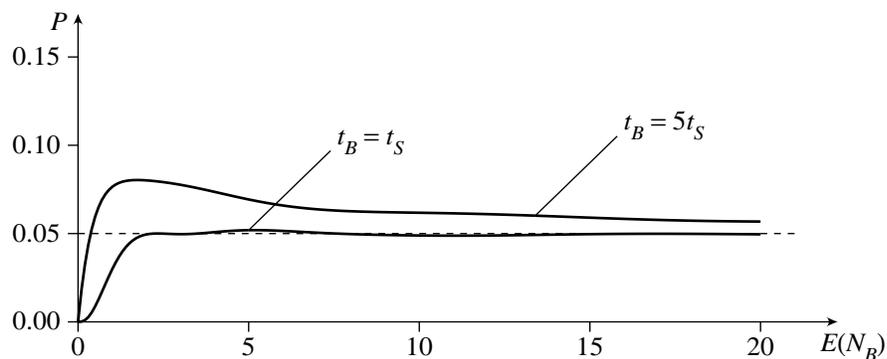


FIGURE 19.15 — Type I error rates for Formula C

2518 If the blank correction involves additional non-Poisson variance, an extra term may be included
 2519 under the radical in Formula C; however, the weights w_S and w_B used to derive the formula are
 2520 not necessarily optimal in this case. (See ISO 2000b for another approach.)

2521 Note that Formulas B and C are equivalent when $t_B = t_S$, because both assign equal weights to the
 2522 blank measurement and the source measurement. In this case, both formulas are also equivalent
 2523 to the formula given by Altshuler and Pasternack (1963).

2524 THE STAPLETON APPROXIMATION

2525 When the mean counts are low and $t_B \neq t_S$, another approximation formula for S_C appears to out-
 2526 perform all of the approximations described above. For small values of the constant d , the
 2527 statistic

2528

$$Z = 2 \left(\sqrt{\frac{N_S + d}{t_S}} - \sqrt{\frac{N_B + d}{t_B}} \right) / \sqrt{\frac{1}{t_S} + \frac{1}{t_B}} \quad (19.108)$$

2529 which involves variance-stabilizing transformations of the Poisson counts N_S and N_B , has a distri-
 2530 bution that is approximately standard normal under the null hypothesis (Stapleton 1999). So, the
 2531 critical value of Z is $z_{1-\alpha}$, the $(1 - \alpha)$ -quantile of the standard normal distribution. From these
 2532 facts one may derive the following expression for the critical net count as a function of N_B .

$$S_C = d \left(\frac{t_S}{t_B} - 1 \right) + \frac{z_{1-\alpha}^2}{4} \left(1 + \frac{t_S}{t_B} \right) + z_{1-\alpha} \sqrt{(N_B + d) \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B} \right)} \quad (19.109)$$

The Stapleton Approximation

2533 When $\alpha = 0.05$, the value $d = 0.4$ appears to be a near-optimal choice. Then for $t_B = t_S$, the
 2534 Stapleton approximation gives the equation

$$S_C = 1.35 + 2.33 \sqrt{N_B + 0.4} \quad (19.110)$$

2535 Figure 19.16 shows the type I error rates for the Stapleton approximation when $\alpha = 0.05$ and
 2536 $d = 0.4$. This approximation gives type I error rates almost identical to those of Formulas B and C
 2537 when $t_B = t_S$, but it has an advantage when $t_B \neq t_S$.

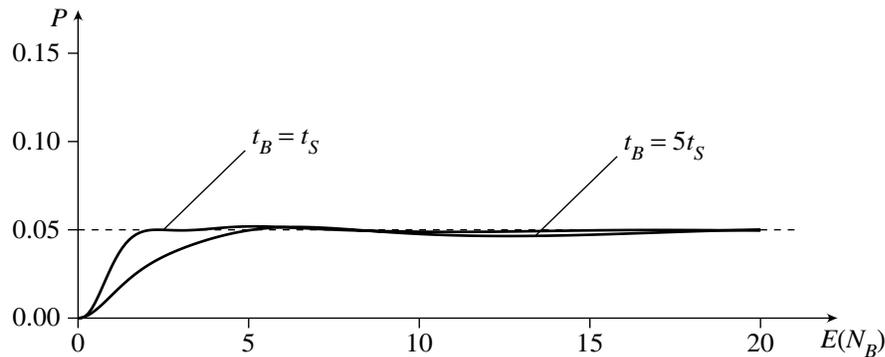


FIGURE 19.16 — Type I error rates for the Stapleton approximation

2538 When $\alpha \neq 0.05$, the value $d = z_{1-\alpha} / 4.112$ appears to give good results ($4.112 = z_{0.95} / 0.4$).

2539 When the blank correction involves a small non-Poisson variance component, a term $(\xi_B^2 t_S^2)$ may
 2540 be included under the radical in Equation 19.109 to account for it.

2541 THE EXACT TEST

2542 Poisson counting statistics also permit an “exact” test for analyte detection, whose type I error
 2543 rate is guaranteed to be *no greater than* the chosen value of α , although it may be less. A random-
 2544 ized version of the test can provide a type I error rate *exactly equal to* α (Nicholson 1963), but
 2545 only the nonrandomized version will be considered here, since its outcome is always based solely
 2546 on the data and not on a random number generator. The test is implemented by rejecting H_0 if and
 2547 only if the following inequality is true.²⁷

$$\sum_{k=N_S}^{N_S+N_B} \binom{N_S+N_B}{k} \left(\frac{t_S}{t_S+t_B} \right)^k \left(\frac{t_B}{t_S+t_B} \right)^{N_S+N_B-k} \leq \alpha \quad (19.111)$$

2548 Nicholson presents the test as a comparison of the gross count N_S to a critical value. The critical
 2549 value \tilde{y}_C is the smallest nonnegative integer n such that²⁸

$$\sum_{k=0}^n \binom{N_S+N_B}{k} \left(\frac{t_S}{t_S+t_B} \right)^k \left(\frac{t_B}{t_S+t_B} \right)^{N_S+N_B-k} \geq 1-\alpha \quad (19.112)$$

2550 The same (nonrandomized) test is implemented by calculating a critical gross count y_C equal to
 2551 the smallest nonnegative integer n such that

$$\sum_{k=0}^n \binom{N_B+k}{N_B} \left(\frac{t_S}{t_S+t_B} \right)^k \geq (1-\alpha) \left(\frac{t_S+t_B}{t_B} \right)^{N_B+1} \quad (19.113)$$

²⁷ The left-hand side of the inequality is a cumulative binomial probability (see Attachment 19A). It also equals

$$I_{\frac{t_S}{t_S+t_B}}(N_S, N_B+1)$$

where $I_x(a, b)$ denotes the incomplete beta function (NBS 1964, Press et al. 1992).

²⁸ To implement the randomized test, calculate the critical value \tilde{y}_C , and, if $N_S > \tilde{y}_C$, reject H_0 , as in the non-randomized test. If $N_S = \tilde{y}_C$, calculate a rejection probability P by subtracting $1 - \alpha$ from the sum on the left-hand side of the inequality (with $n = N_S$) and dividing the difference by the summation’s last term

$$\binom{N_S+N_B}{N_S} \left(\frac{t_S}{t_S+t_B} \right)^{N_S} \left(\frac{t_B}{t_S+t_B} \right)^{N_B}$$

Then reject H_0 with probability P .

2552 Then the critical net count S_C equals $y_C - N_B(t_S/t_B)$. (Note that Inequality 19.113 is intended for
 2553 use when N_B is small.) Table G.4 in Appendix G lists critical values y_C for $\alpha = 0.01$ and 0.05 and
 2554 for integral values of the count time ratio t_B/t_S ranging from 1 to 5.

2555 Figure 19.17 shows the type I error rates for the nonrandomized exact test. (The type I error rate
 2556 for the randomized version of the test equals 0.05 everywhere.)

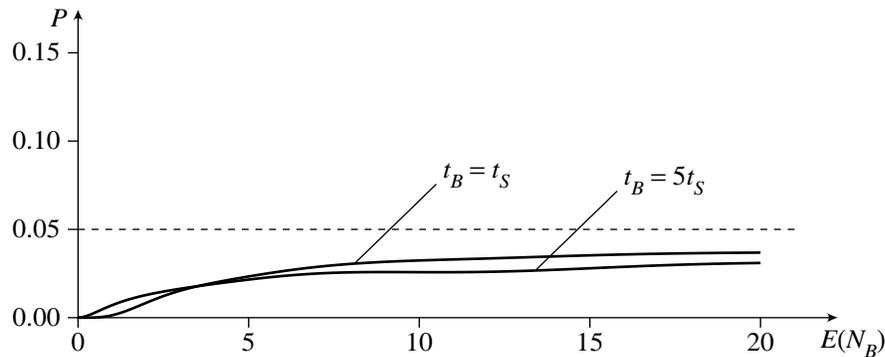


FIGURE 19.17 — Type I error rates for the nonrandomized exact test

2557

EXAMPLE

2558 **Problem:** A 6000-s blank measurement is performed on a proportional counter and 108 beta
 2559 counts are observed. A test source is to be counted for 3000 s. Estimate the critical value of the
 2560 net count when $\alpha = 0.05$.

2561 **Solution:** Formula A gives the result

$$\begin{aligned}
 S_C &= z_{1-\alpha} \sqrt{N_B \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B}\right)} \\
 &= 1.645 \sqrt{108 \left(\frac{3000}{6000}\right) \left(1 + \frac{3000}{6000}\right)} \\
 &= 14.8 \text{ counts.}
 \end{aligned}$$

2563

Formula B is not recommended.

2564 Formula C gives the result

$$\begin{aligned}
 S_C &= \frac{z_{1-\alpha}^2 t_S}{2t_B} + z_{1-\alpha} \sqrt{\frac{z_{1-\alpha}^2 t_S^2}{4t_B^2} + N_B \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B}\right)} \\
 &= \frac{1.645^2(3000)}{2(6000)} + 1.645 \sqrt{\frac{1.645^2(3000)^2}{4(6000)^2} + 108 \left(\frac{3000}{6000}\right) \left(1 + \frac{3000}{6000}\right)} \\
 &= 15.5 \text{ counts.}
 \end{aligned}$$

2566 The Stapleton approximation (with $d = 0.4$) gives the result

$$\begin{aligned}
 S_C &= d \left(\frac{t_S}{t_B} - 1\right) + \frac{z_{1-\alpha}^2}{4} \left(1 + \frac{t_S}{t_B}\right) + z_{1-\alpha} \sqrt{(N_B + d) \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B}\right)} \\
 &= 0.4 \left(\frac{3000}{6000} - 1\right) + \frac{1.645^2}{4} \left(1 + \frac{3000}{6000}\right) + 1.645 \sqrt{(108 + 0.4) \left(\frac{3000}{6000}\right) \left(1 + \frac{3000}{6000}\right)} \\
 &= 15.6 \text{ counts.}
 \end{aligned}$$

2568 The exact test gives the result $y_C = 70$ counts (the entry in Table G.4 for $\alpha = 0.05$, $t_B / t_S = 2$,
 2569 and $N_B = 108$), which implies that

$$S_C = 70 - (108)(3000 / 6000) = 16 \text{ counts.}$$

2571 COMPARISONS

2572 Although Formula A gives the highest type I error rates of all the formulas described above in the
 2573 pure Poisson counting scenario, it is the formula that can be adapted most easily for dealing with
 2574 interferences. It can also be modified to reduce the very high type I error rates at low blank levels
 2575 (by adding 1 or 2 to the number of blank counts N_B under the radical). Formula B cannot be
 2576 recommended. When the pure Poisson model is valid, Formula C gives better results than either
 2577 A or B, but the Stapleton approximation appears to give the most predictable type I error rates of
 2578 all. Nicholson's exact test is the most complicated of the tests and requires either software or
 2579 lookup tables to be practical, but it is the only one of the tests whose type I error rate is guaran-
 2580 teed not to exceed the chosen significance level. Achieving the chosen significance level exactly
 2581 appears to require the randomized version of Nicholson's test.

2582 **19D.3 Calculation of the Minimum Detectable Concentration**

2583 The minimum detectable concentration, or MDC, was defined earlier as the concentration of
 2584 analyte, x_D , that must be present in a laboratory sample to give a probability $1 - \beta$ of obtaining a
 2585 measured response greater than its critical value. Equivalently, the MDC is defined as the analyte
 2586 concentration x_D that satisfies the relation

$$\Pr[\hat{S} \leq S_C | X = x_D] = \beta \quad (19.114)$$

2587 where the expression $\Pr[\hat{S} \leq S_C | X = x_D]$ may be read as “the probability that the net signal \hat{S}
 2588 does not exceed its critical value S_C when the true concentration X is equal to x_D .”

2589 **19D.3.1 The Minimum Detectable Net Instrument Signal**

2590 The MDC may be estimated by calculating the minimum detectable value of the net instrument
 2591 signal, S_D , and converting the result to a concentration. The minimum detectable value of the net
 2592 instrument signal is defined as the mean value of the net signal that gives a specified probability
 2593 $1 - \beta$ of yielding an observed signal greater than its critical value S_C . Thus,

$$\Pr[\hat{S} \leq S_C | S = S_D] = \beta \quad (19.115)$$

2594 where S denotes the true mean net signal.

2595 **19D.3.2 Normally Distributed Signals**

2596 If the net signal \hat{S} is normally distributed and its estimated standard deviation $\hat{\sigma}_0$ under H_0 is
 2597 determined from a statistical evaluation with ν degrees of freedom (e.g., $n = \nu + 1$ replicate blank
 2598 measurements), then the critical value of \hat{S} is

$$S_C = t_{1-\alpha}(\nu) \hat{\sigma}_0 \quad (19.116)$$

2599 Then, if the variance of \hat{S} is constant at all concentrations, the minimum detectable value of the
 2600 signal is given by

$$S_D = \delta_{\alpha, \beta, \nu} \sigma_0 \quad (19.117)$$

2601 where $\delta_{\alpha,\beta,v}$ denotes the non-centrality parameter of the non-central t -distribution with v degrees
 2602 of freedom. The parameter $\delta_{\alpha,\beta,v}$ is such that

$$t'_{\beta}(v, \delta_{\alpha,\beta,v}) = t_{1-\alpha}(v) \quad (19.118)$$

2603 where $t'_{\beta}(v, \delta_{\alpha,\beta,v})$ denotes the β -quantile of the non-central t -distribution. The non-centrality
 2604 parameter $\delta_{\alpha,\beta,v}$ may be approximated by

$$\delta_{\alpha,\beta,v} \approx t' \left(1 - \frac{1}{4v} \right) + z_{1-\beta} \sqrt{1 + \frac{t'^2}{2v}}, \quad t' = t_{1-\alpha}(v) \quad (19.119)$$

2605 which is based on an approximation for the non-central t distribution function (NBS 1964).
 2606 When $\alpha = \beta = 0.05$ and $v \geq 4$, the non-centrality parameter is also approximated adequately by
 2607 $t_{0.95}(v) \times 8v / (4v + 1)$ (Currie 1997).

2608 Conceptually the standard deviation $\hat{\sigma}_0$ used to calculate the critical value S_C is only an estimate
 2609 and therefore can be considered a random variable. If it were the true standard deviation, the cor-
 2610 rect multiplier used to calculate S_C would be $z_{1-\alpha}$, not $t_{1-\alpha}(v)$. However, the standard deviation
 2611 used to calculate S_D is, conceptually at least, the true standard deviation σ_0 , even if its value is not
 2612 known exactly. The true standard deviation may be estimated by $\hat{\sigma}_0$, but since the estimator $\hat{\sigma}_0$ is
 2613 biased, a correction factor should be used for v less than about 20. An unbiased estimator for σ_0 is
 2614 $\hat{\sigma}_0 / c_4$, where

$$c_4 = \frac{\Gamma\left(\frac{v+1}{2}\right)}{\Gamma\left(\frac{v}{2}\right)} \sqrt{\frac{2}{v}} \quad (19.120)$$

2615 and where Γ denotes the *gamma function* (NBS 1964). The gamma function is easily computed
 2616 in software (Press et al. 1992), but c_4 is also approximated well by $4v / (4v + 1)$, and values of c_4
 2617 are commonly tabulated in references for statistical quality control (whence the notation c_4 is
 2618 borrowed). Then S_D is estimated by

$$S_D = \delta_{\alpha,\beta,v} \frac{\hat{\sigma}_0}{c_4} \quad (19.121)$$

TABLE 19.5 — Bias factor for the experimental standard deviation

v	c_4	v	c_4	v	c_4	v	c_4
1	0.79788	11	0.97756	21	0.98817	31	0.99197
2	0.88623	12	0.97941	22	0.98870	32	0.99222
3	0.92132	13	0.98097	23	0.98919	33	0.99245
4	0.93999	14	0.98232	24	0.98964	34	0.99268
5	0.95153	15	0.98348	25	0.99005	35	0.99288
6	0.95937	16	0.98451	26	0.99043	36	0.99308
7	0.96503	17	0.98541	27	0.99079	37	0.99327
8	0.96931	18	0.98621	28	0.99111	38	0.99344
9	0.97266	19	0.98693	29	0.99142	39	0.99361
10	0.97535	20	0.98758	30	0.99170	40	0.99377

2619 which is approximately $2 t_{0.95}(v) \hat{\sigma}_0$, or $2 S_C$, when $\alpha = \beta = 0.05$ and $v \geq 4$. Values of c_4 for $v = 1$ to
 2620 40 are listed in Table 19.5.
 2621 Lower and upper confidence limits for S_D may be calculated using the equations

$$S_{D,lower} = \delta_{\alpha,\beta,v} \frac{\hat{\sigma}_0}{\sqrt{\chi_{1-\gamma/2}^2(v) / v}} \quad \text{and} \quad S_{D,upper} = \delta_{\alpha,\beta,v} \frac{\hat{\sigma}_0}{\sqrt{\chi_{\gamma/2}^2(v) / v}} \quad (19.122)$$

2622 where $\chi_p^2(v)$ denotes the p -quantile of the chi-square distribution with v degrees of freedom and γ
 2623 denotes the desired confidence coefficient (see Table G.3 in Appendix G).

2624 If the variance of \hat{S} is not constant but increases with the mean signal S , the minimum detectable
 2625 net signal is determined implicitly by the equation

$$t_{\beta} \left(v, \frac{S_D}{\sigma_D} \right) = t_{1-\alpha}(v) \frac{\sigma_0}{\sigma_D} \quad (19.123)$$

2626 where σ_D denotes the standard deviation of \hat{S} when $S = S_D$. An iterative algorithm, such as the
 2627 one shown below, may be needed to solve the equation for S_D .

- 2628 1. Set $\sigma_0 = \sqrt{\sigma^2(\hat{S} | S = 0)}$

- 2629 2. Set $S_D = t_{1-\alpha}(v)\sigma_0$
- 2630 3. **repeat**
- 2631 4. Set $\sigma_D = \sqrt{\sigma^2(\hat{S} | S = S_D)}$
- 2632 5. Find the value of δ such that $t_{\beta}'(v, \delta) = t_{1-\alpha}(v) \sigma_0 / \sigma_D$
- 2633 6. Set $h = S_D$
- 2634 7. Set $S_D = \delta \sigma_D$
- 2635 8. **until** $|S_D - h|$ is sufficiently small
- 2636 9. **output** the solution S_D

2637 The value of the non-centrality parameter δ in Step 5 may be approximated by

$$\delta \approx t' \left(1 - \frac{1}{4v} \right) + z_{1-\beta} \sqrt{1 + \frac{t'^2}{2v}}, \quad t' = t_{1-\alpha}(v) \frac{\sigma_0}{\sigma_D} \quad (19.124)$$

2638 When $\hat{\sigma}_0$ is determined by any means other than a statistical evaluation, S_D must be calculated
 2639 differently.

2640 19D.3.3 Poisson Counting

2641 Another equation for S_D , which was described in Section 19.7.2.2, is

$$S_D = S_C + z_{1-\beta} \sqrt{\sigma^2(\hat{S} | S = S_D)} \quad (19.125)$$

2642 where $S_C = z_{1-\alpha} \sigma_0$ and $\sigma^2(\hat{S} | S = S_D)$ denotes the variance of the measured signal \hat{S} when the true
 2643 mean signal S equals S_D . This equation is the basis for formulas that are commonly used for S_D
 2644 when the Poisson-normal approximation is assumed. Regardless of whether the signal follows
 2645 the pure Poisson model or has non-Poisson variance, the function $\sigma^2(\hat{S} | S = S_D)$ can often be
 2646 expressed in the form

$$\sigma^2(\hat{S}) = aS^2 + bS + c \quad (19.126)$$

2647 where S denotes the true mean net signal and the constants a , b , and c do not depend on S . In this
 2648 case, the minimum detectable net signal is given approximately by

$$S_D = \frac{1}{I_\beta} \left(S_C + \frac{z_{1-\beta}^2 b}{2} + z_{1-\beta} \sqrt{b S_C + \frac{z_{1-\beta}^2 b^2}{4} + a S_C^2 + I_\beta c} \right) \quad (19.127)$$

2649 where $I_\beta = 1 - z_{1-\beta}^2 a$.

2650 Equation 19.125 is often used even when S_C is calculated using one of the formulas presented
 2651 above for low-background Poisson counting, with $R_B t_B$ substituted for the blank count N_B , but in
 2652 this case S_D may be underestimated because of the fact that the calculated value of S_C varies from
 2653 measurement to measurement. One option for obtaining a more conservative estimate of S_D is to
 2654 substitute a conservative value of S_C , which will be denoted here by $[S_C]$. For Poisson counting,
 2655 one method of obtaining $[S_C]$ is to use the value of S_C calculated from the largest blank count N_B
 2656 likely to be observed, given the assumed mean blank count rate R_B (e.g., use Table 19.4 with $R_B t_B$
 2657 replacing $R_B t_S$ and N_B replacing y_C in the column headings). To calculate S_D , one may substitute
 2658 $[S_C]$ for S_C in Equation 19.127.

2659 Note that $[S_C]$ is not used to make detection decisions. It is used only to calculate S_D .

2660 For example, suppose $\alpha = \beta = 0.05$, the assumed mean blank count rate is $R_B = 8 \times 10^{-4}$ cps, and
 2661 the blank count time is $t_B = 6000$ s. Then $R_B t_B = 4.8$ counts. Using Table 19.4, one finds 4.8 in
 2662 the first column between 4.695 and 5.425, and reads the value 9 from the second column. So, 9 is
 2663 the largest value of N_B likely to be observed when measuring a blank. Now, if Stapleton's
 2664 approximation is used to calculate \tilde{S}_C when making a detection decision, the value of $[S_C]$ used
 2665 to calculate S_D is given by the following equation.

$$[S_C] = 0.4 \left(\frac{t_S}{t_B} - 1 \right) + \frac{1.645^2}{4} \left(1 + \frac{t_S}{t_B} \right) + 1.645 \sqrt{(9 + 0.4) \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B} \right)} \quad (19.128)$$

2667 So, if $t_S = t_B$, then $[S_C] = 8.48$ counts. If $R_B t_B$ (4.8 counts) were used as the blank count instead,
 2668 $[S_C]$ would be only 6.66 counts.

2669 PURE POISSON COUNTING

2670 When the pure Poisson model is assumed and Formula A is used for the critical value, if the
 2671 critical value, S_C , is determined from a sufficiently large total number of counts and if $\alpha = \beta$, the
 2672 minimum detectable net signal S_D is given by the following simple equation.

$$S_D = z_{1-\beta}^2 + 2S_C \quad (19.129)$$

2673 More generally, if Formula A or C is used to calculate the critical net count S_C , then S_D may be
 2674 determined from Equation 19.127 using the following values for a , b , and c .

2675

$$a = 0 \quad b = 1 \quad c = R_B t_S \left(1 + \frac{t_S}{t_B} \right)$$

2676 The resulting formula for S_D is

$$S_D = S_C + \frac{z_{1-\beta}^2}{2} + z_{1-\beta} \sqrt{\frac{z_{1-\beta}^2}{4} + S_C + R_B t_S \left(1 + \frac{t_S}{t_B} \right)} \quad (19.130)$$

2677 As previously noted, counting data never follow the Poisson model exactly. Variable factors such
 2678 as source geometry and placement, counting efficiency, and subsampling variance tend to
 2679 increase a , while interferences and background instability tend to increase c .

2680 THE STAPLETON APPROXIMATION

2681 When the Stapleton approximation is used for S_C , the minimum detectable net count S_D may be
 2682 calculated using Equation 19.130, but when the Poisson model is valid, a better estimate is given
 2683 by the formula

$$S_D = \frac{(z_{1-\alpha} + z_{1-\beta})^2}{4} \left(1 + \frac{t_S}{t_B} \right) + (z_{1-\alpha} + z_{1-\beta}) \sqrt{R_B t_S \left(1 + \frac{t_S}{t_B} \right)} \quad (19.131)$$

2684 Equation 19.131 also gives a better approximation of S_D even when Formula C is used for the
 2685 critical value as long as the ratio of count times t_B / t_S is not too far from 1 (see Table 19.6). It is
 2686 recommended by ISO 11929-1 (ISO 2000a) in a slightly different but equivalent form.

2687 When $\alpha = \beta = 0.05$ and $t_B = t_S$, the preceding equation becomes

$$S_D = 5.41 + 4.65\sqrt{R_B t_S} \quad (19.132)$$

2688 The Stapleton approximations for S_C and S_D give very predictable type I and type II errors when
 2689 the only measurement variance is Poisson.

2690 When the Poisson model is incomplete because of excess relative variance ($a > 0$), one can use
 2691 Equation 19.127 with appropriate values for a , b , and c . However, a somewhat better estimate of
 2692 S_D can be obtained. The calculation is more involved.

$$S_D = \frac{b'^2 - 2a'c' + b'\sqrt{b'^2 - 4a'c'}}{2a'^2} - R_B t_S \quad (19.133)$$

2693 where

$$2694 \quad a' = 1 - \frac{z_{1-\beta}^2 a}{4}$$

$$2695 \quad b' = 2\sqrt{R_B t_S} + z_{1-\alpha} \sqrt{1 + \frac{t_S}{t_B}}$$

$$2696 \quad c' = R_B t_S + \frac{z_{1-\alpha}^2 - z_{1-\beta}^2}{4} \left(1 + \frac{t_S}{t_B}\right) + z_{1-\alpha} \sqrt{R_B t_S \left(1 + \frac{t_S}{t_B}\right)}$$

2697 PRECISE CALCULATION OF S_D

2698 When the Poisson model is valid, the mean blank count rate R_B and the analyte detection criteria
 2699 completely determine S_D . So, in principle, a computer program can be written to calculate S_D
 2700 precisely. The calculation is most easily described when the critical net count is expressed in
 2701 terms of N_B but not N_S (e.g., S_C as defined by Formulas A–C, the Stapleton approximation, and
 2702 the exact test). Then, at any specified value S of the mean net signal, the power of the detection
 2703 test can be computed using the expression:

$$\text{Power} = 1 - \exp(-R_B(t_S + t_B) - S) \sum_{n=0}^{\infty} \frac{(R_B t_B)^n}{n!} \sum_{k=0}^{\lfloor y_C(n) \rfloor} \frac{(R_B t_S + S)^k}{k!} \quad (19.134)$$

2704 where $y_C(n)$ denotes the value of y_C (or $S_C + N_B t_S / t_B$) when $N_B = n$. Terms of the infinite sum
 2705 must be accumulated only until the cumulative Poisson probability, $e^{-R_B t_B} \sum_{m=0}^n (R_B t_B)^m / m!$,
 2706 approaches 1. Given a software procedure to compute Equation 19.134, the value of S_D may be
 2707 determined using an iterative algorithm, such as Newton's method or bisection, which calculates
 2708 the power at various trial values of S until the correct value is found where the power equals
 2709 $1 - \beta$ (e.g. see Burden and Faires 1993).

2710 A procedure of the type described above generated the true values of S_D for Table 19.6, which
 2711 shows both the estimated and true values of S_D obtained when Formulas A and C and the
 2712 Stapleton approximation are used for the critical value. The estimated values of S_D in this table
 2713 are based on values of S_C calculated using the true mean net count, not the upper bound $[N_B]$. The
 2714 use of $[N_B]$ would produce larger estimates.

2715 PRECISE CALCULATION OF x_D

2716 Suppose the analyte concentration X is calculated by dividing the net signal S by the sensitivity A ,
 2717 where A varies considerably or there is considerable subsampling variance, but the signal is
 2718 otherwise adequately described by the Poisson model. If one can assume that A has a particular
 2719 distribution, such as a rectangular or triangular distribution, then it is possible to calculate x_D pre-
 2720 cisely in software, although the mathematics is less straightforward than that needed to calculate
 2721 S_D in the preceding section. At any specified concentration x , the detection power equals

$$\text{Power} = 1 - e^{-R_B t_B} \sum_{n=0}^{\infty} \frac{(R_B t_B)^n}{n!} \sum_{k=0}^{\lfloor y_C(n) \rfloor} f(k; x) \quad (19.135)$$

2722 where $f(k; x)$ is the probability that the gross count will equal k when the concentration is x . For
 2723 example, if A has a rectangular distribution with mean μ_A and half-width δ , then

$$f(k; x) = \frac{P(k + 1, R_B t_S + (\mu_A + \delta)x) - P(k + 1, R_B t_S + (\mu_A - \delta)x)}{2\delta x} \quad (19.136)$$

2724 where $P(\cdot, \cdot)$ denotes the incomplete gamma function. Other combinations of the incomplete
 2725 gamma function appear when different polygonal distributions are assumed (e.g., triangular).

TABLE 19.6 — Estimated and true values of S_D ($t_B = t_S$)

Mean Blank Count	Formula A		Formula C		Stapleton	
	Estimated	True	Estimated	True	Estimated	True
0	2.706	2.996	7.083	6.296	5.411	6.296
1	7.358	8.351	9.660	10.095	10.063	10.095
2	9.285	10.344	11.355	12.010	11.991	12.010
3	10.764	11.793	12.719	13.551	13.469	13.551
4	12.010	13.021	13.894	14.826	14.716	14.826
5	13.109	14.091	14.942	15.930	15.814	15.930
6	14.101	15.076	15.897	16.902	16.807	16.902
7	15.015	16.028	16.780	17.785	17.720	17.785
8	15.864	16.945	17.605	18.614	18.570	18.614
9	16.663	17.804	18.383	19.406	19.368	19.406
10	17.418	18.595	19.120	20.170	20.123	20.170
11	18.136	19.324	19.823	20.903	20.841	20.903
12	18.822	20.002	20.496	21.602	21.527	21.602
13	19.480	20.642	21.142	22.267	22.185	22.267
14	20.113	21.257	21.764	22.900	22.819	22.900
15	20.724	21.854	22.366	23.506	23.430	23.506
16	21.315	22.438	22.948	24.091	24.020	24.091
17	21.888	23.010	23.513	24.657	24.593	24.657
18	22.444	23.569	24.062	25.206	25.149	25.206
19	22.985	24.116	24.596	25.738	25.690	25.738
20	23.511	24.649	25.116	26.252	26.217	26.252

2726 A precise power calculation of this type was performed to evaluate the results derived in the
2727 example in Attachment 19E assuming an approximately normal distribution for the subsampling
2728 error. The assumption of a normal distribution is nonsensical unless the relative standard devia-
2729 tion of A is small (because A is positive), and in the latter case, the assumption of a triangular
2730 distribution, or even a rectangular distribution, gives approximately the same result.

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2775 **ATTACHMENT 19E**
2776 **Example Calculations**

2777 **19E.1 Overview**

2778 The following example shows how to calculate the combined standard uncertainty, critical net
2779 signal, minimum detectable concentration (MDC), and minimum quantifiable concentration
2780 (MQC) for a typical radioanalytical measurement.

2781 **19E.2 Sample Collection and Analysis**

2782 A soil sample is analyzed for $^{239/240}\text{Pu}$ and ^{238}Pu by alpha spectrometry.

- 2783 • The sample is collected on July 10, 1999, at 11:17 am EDT, and shipped to a laboratory
2784 for analysis.
- 2785 • The entire laboratory sample is dried, weighed, and ground to a maximum particle size of
2786 0.2 mm. The dry weight is approximately 2 kg.
- 2787 • The prepared sample is homogenized, and a test portion is removed by increments. The
2788 documented procedure requires a test portion of approximately 0.5 g.
- 2789 • The test portion is weighed and the mass is found to be 0.5017 g. The standard
2790 uncertainty of the mass, including contributions from repeatability, linearity, day-to-day
2791 variability, and the balance calibration, is estimated to be 2.2×10^{-4} g.
- 2792 • A 1-mL aliquant of ^{242}Pu tracer is added to the test portion. The concentration of the
2793 tracer solution has previously been measured as $0.0705 \text{ Bq mL}^{-1}$ with a standard
2794 uncertainty of $0.0020 \text{ Bq mL}^{-1}$ on June 30, 1999, at 11:00 am CDT. The aliquant is
2795 dispensed by a pipet, whose dispensed volume has a combined standard uncertainty
2796 previously determined to be 0.0057 mL.
- 2797 • After fusion, dissolution, chemical purification, and coprecipitation, a test source on a
2798 stainless steel planchet is prepared for counting in an alpha spectrometer.
- 2799 • The efficiency of the spectrometer for the chosen geometry, which is assumed to be con-
2800 stant over the range of alpha energies of interest, has previously been measured as 0.2805
2801 with a standard uncertainty of 0.0045.

- 2802 • A blank source is counted in the spectrometer for 60,000 s. The blank consists of a filter
2803 mounted on a planchet in the same geometry as the test source. In the ^{242}Pu region of
2804 interest, 2 counts are measured; and in the ^{238}Pu region of interest, 0 counts are measured.
2805 Historical data for this and similar spectrometers at the laboratory indicate that the back-
2806 ground is stable between measurements.
- 2807 • The test source is placed in the spectrometer and counted for 60,000 s, beginning on
2808 August 24, 1999, at 4:47 pm CDT. In the ^{242}Pu region of interest, 967 counts are meas-
2809 ured; and in the ^{238}Pu region of interest, 75 counts are measured.
- 2810 • It is assumed that there is no detectable plutonium in the reagents; however, a method
2811 blank is analyzed simultaneously using a different spectrometer to check for contamina-
2812 tion of reagents and glassware.)

2813 In this example the measurand will be the mean activity concentration, or massic activity, of
2814 ^{238}Pu in the 2-kg sample (dry weight) at the time of collection.

2815 **19E.3 The Measurement Model**

2816 The following notation will be used:

- 2817 M_S is the mass of the test portion (0.5017 g)
2818 T is the tracer activity concentration ($0.1205 \text{ Bq mL}^{-1}$)
2819 V_t is the tracer aliquant volume (1 mL)
2820 t_B is the blank count time (60,000 s)
2821 t_S is the count time for the test source (60,000 s)
2822 N_S is the total count in a region of interest when the source is counted (^{238}Pu or ^{242}Pu)
2823 N_B is the count in a region of interest when the blank is counted (^{238}Pu or ^{242}Pu)
2824 R is the fraction of alphas with measured energy in the region of interest (^{238}Pu or ^{242}Pu)
2825 D is the decay-correction factor (^{238}Pu or ^{242}Pu)
2826 ϵ is the alpha counting efficiency
2827 Y is the plutonium chemical yield fraction
2828 F_S is the subsampling factor (estimated as 1.00 with a Type B standard uncertainty of
2829 0.05)
2830 X is the ^{238}Pu activity concentration in the dried laboratory sample, decay-corrected to
2831 the time of collection

2832 Subscripts will be used to distinguish between quantities associated with particular regions of
2833 interest (^{238}Pu or ^{242}Pu).

2834 The decay-correction factor for either isotope is calculated as follows:

2835
$$D = e^{-\lambda t_D} \frac{1 - e^{-\lambda t_S}}{\lambda t_S}$$

2836 where λ is the decay constant (s^{-1}) and t_D is the time between collection and the start of the
 2837 counting measurement (3,911,400 s). Since λt_S is small for both isotopes in this example, D may
 2838 be approximated accurately by

2839
$$D = e^{-\lambda(t_D + t_S/2)}$$

2840 The half-lives of ^{238}Pu and ^{242}Pu are 87.75 y and 375,800 y, respectively. So,

2841
$$D_{238} = \exp\left(\frac{-\ln 2}{87.75 \cdot 365.25 \cdot 86,400} \left(3,911,400 + \frac{60,000}{2}\right)\right) = 0.9990$$

2842 and $D_{242} = 1.000$.

2843 Dead time is negligible in this example; so, no distinction is made between the real time and the
 2844 live time. If the real time were greater than the live time, the correction for decay during the
 2845 counting period would be based on the real time.

2846 The fraction of alphas of each isotope actually measured in the nominal region of interest is esti-
 2847 mated to lie between 0.96 and 1.00. A rectangular distribution is assumed, with center at 0.98
 2848 and half-width equal to 0.02. Then the Type B standard uncertainties of R_{238} and R_{242} are

2849
$$u(R_{238}) = u(R_{242}) = \frac{0.02}{\sqrt{3}} = 0.01155$$

2850 The chemical yield of plutonium is calculated using the model

2851
$$Y = \frac{N_{S,242}/t_S - N_{B,242}/t_B}{TV_t \epsilon R_{242} D_{242}}$$

2852 Then the following model is used to estimate the measurand.

2853
$$X = \frac{N_{S,238} / t_S - N_{B,238} / t_B}{M_S Y \epsilon R_{238} D_{238} F_S}$$

2854 When numerical values are inserted,

$$Y = \frac{967 / 60,000 - 2 / 60,000}{0.0705 \cdot 1 \cdot 0.2805 \cdot 0.98 \cdot 1} = 0.82990$$

$$X = \frac{75 / 60,000 - 0 / 60,000}{0.5017 \cdot 0.82990 \cdot 0.2805 \cdot 0.98 \cdot 0.9990 \cdot 1.00} = 0.010932 \text{ Bq g}^{-1}$$

(or 10.932 Bq kg⁻¹)

2855 **19E.4 The Combined Standard Uncertainty**

2856 The efficiency ϵ effectively cancels out of the equation for X , because it is multiplied by the yield
 2857 Y and also appears as a factor in the denominator of the expression for Y (see also Section
 2858 19.6.5). Therefore, the uncertainty of ϵ has no effect on the uncertainty of X . When using the
 2859 uncertainty propagation formula to calculate the combined standard uncertainty of X , one might
 2860 include a covariance term for $u(Y, \epsilon)$ to account for the relationship between the measured values
 2861 of Y and ϵ , but it is simpler to treat $Y\epsilon$ as one variable. Application of the uncertainty propagation
 2862 formula (Section 19.5.3) to the equations above then gives the following:

2863
$$u_c^2(Y\epsilon) = \frac{u^2(N_{S,242}) / t_S^2 + u^2(N_{B,242}) / t_B^2}{T^2 V_t^2 R_{242}^2 D_{242}^2} + (Y\epsilon)^2 \left(\frac{u^2(T)}{T^2} + \frac{u^2(V_t)}{V_t^2} + \frac{u^2(R_{242})}{R_{242}^2} \right)$$

2864
$$u_c^2(X) = \frac{u^2(N_{S,238}) / t_S^2 + u^2(N_{B,238}) / t_B^2}{M_S^2 (Y\epsilon)^2 R_{238}^2 D_{238}^2} + X^2 \left(\frac{u^2(M_S)}{M_S^2} + \frac{u^2(Y\epsilon)}{(Y\epsilon)^2} + \frac{u^2(R_{238})}{R_{238}^2} + \frac{u^2(F_S)}{F_S^2} \right)$$

2865 All other input estimates are assumed to be uncorrelated.

2866 Note that $u^2(F_S)$ is the subsampling variance associated with taking a small test portion
 2867 (0.5017 g) from a much larger sample (2 kg). A default value is used here for this variance
 2868 component. However, Appendix F provides more information about subsampling errors and
 2869 methods for estimating their variances.

2870 Since extremely low counts are possible, each Poisson counting variance in this example will be
 2871 estimated by the number of observed counts plus one (see Section 19.5.2.2 and Section 19C.3 of
 2872 Attachment 19C). So, for example, $u(N_{B,238})$ equals one, not zero.

2873 Table 19.7 summarizes the input estimates and their standard uncertainties.

TABLE 19.7 — 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
T	0.0705	0.0020	Bq mL ⁻¹	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	0.05	none	B
D_{238}	0.9990	Negligible	none	B
D_{242}	1.0000	Negligible	none	B

2874 Other possible sources of uncertainty in alpha spectrometry measurements include the following:

- 2875 • uncertainties in half-lives and decay times
- 2876 • spillover and baseline interferences caused by poor peak resolution
- 2877 • incomplete equilibration of tracer and analyte before chemical separation
- 2878 • changing instrument background
- 2879 • dependence of counting efficiency on alpha energy

2880 These uncertainties are evaluated as negligible in this example. Uncertainties associated with
 2881 half-lives and decay times are negligible, because the decay times in the example are much
 2882 shorter than the half-lives; but in practice one should confirm that any other uncertainties are
 2883 small enough to be neglected.

2884 When numerical values are inserted into the formulas

$$2885 \quad u_c^2(Y\varepsilon) = \frac{968 / 60,000^2 + 3 / 60,000^2}{0.0705^2 \cdot 1^2 \cdot 0.98^2 \cdot 1^2} + (0.82990 \cdot 0.2805)^2 \left(\frac{0.0020^2}{0.0705^2} + \frac{0.0057^2}{1^2} + \frac{0.01155^2}{0.98^2} \right)$$

$$= 0.0001094007 = 0.01046^2$$

2886 and

$$2887 \quad u_c^2(X) = \frac{76 / 60,000^2 + 1 / 60,000^2}{0.5017^2 \cdot (0.82990 \cdot 0.2805)^2 \cdot 0.98^2 \cdot 0.9990^2}$$

$$+ 0.010932^2 \left(\frac{(2.2 \times 10^{-4})^2}{0.5017^2} + \frac{0.01046^2}{0.82990^2 \cdot 0.2805^2} + \frac{0.01155^2}{0.98^2} + \frac{0.05^2}{1.00^2} \right)$$

$$= 2.1926 \times 10^{-6} = 0.0014808^2$$

2888 So, $u_c(X) = 0.00148 \text{ Bq g}^{-1}$ or 1.48 Bq kg^{-1} . If the concentration is to be reported with an expanded uncertainty calculated from the combined standard uncertainty $u_c(X)$ and a coverage factor
 2889 $k = 2$, the result should appear (in SI units) as $10.9 \pm 3.0 \text{ Bq kg}^{-1}$ (dry weight).
 2890

2891 **19E.5 The Critical Net Count**

2892 Chapter 19 discusses several methods for estimating the critical net count S_C . In this example, the
 2893 observed blank count is zero; so, the mean blank count is obviously very low, and nonnormal
 2894 Poisson counting statistics may be assumed. Sections 19E.5.1 through 19E.5.4 below show how
 2895 to apply the formulas discussed in Section 19D.2.2 for Poisson counting measurements,
 2896 assuming a significance level of $\alpha = 0.05$.

2897 **19E.5.1 Formula A**

2898 Formula A is not recommended when the blank count is extremely low, as in this example. How-
 2899 ever, if Formula A is used, it gives the following estimate of the critical value of the net count.

$$\begin{aligned}
 S_C &= z_{1-\alpha} \sqrt{N_{B,238} \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B}\right)} \\
 &= 1.645 \sqrt{(0)(1)(2)} \\
 &= 0 \text{ counts}
 \end{aligned}$$

2900

2901 Since the net count 75 exceeds the critical net count 0, the analyte ^{238}Pu is considered “detected.”

2902 19E.5.2 Formula C

2903 Using Formula C, one obtains

$$\begin{aligned}
 S_C &= \frac{z_{1-\alpha}^2 t_S}{2t_B} + z_{1-\alpha} \sqrt{\frac{z_{1-\alpha}^2 t_S^2}{4t_B^2} + N_{B,238} \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B}\right)} \\
 &= \frac{1.645^2}{2} (1) + 1.645 \sqrt{\frac{1.645^2}{4} (1)^2 + (0)(1)(2)} \\
 &= 2.71 \text{ counts}
 \end{aligned}$$

2904 Since $75 > 2.71$, the analyte is considered detected.

2905 19E.5.3 The Stapleton Approximation

2906 Using the Stapleton approximation, the critical net count is calculated as follows.

$$\begin{aligned}
 S_C &= 0.4 \left(\frac{t_S}{t_B} - 1 \right) + \frac{z_{1-\alpha}^2}{4} \left(1 + \frac{t_S}{t_B} \right) + z_{1-\alpha} \sqrt{(N_{B,238} + 0.4) \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B} \right)} \\
 &= 0.4(0) + \frac{1.645^2}{4} (2) + 1.645 \sqrt{(0 + 0.4)(1)(2)} \\
 &= 2.82 \text{ counts}
 \end{aligned}$$

2907 Since $75 > 2.82$, the analyte is considered detected.

2908 19E.5.4 Exact Test

2909 When the exact test is used, the critical value of the source count $N_{S,238}$ is the smallest nonnega-
 2910 tive integer y_C such that

$$\sum_{k=0}^{y_C} \binom{N_{B,238} + k}{N_{B,238}} \left(\frac{t_S}{t_B + t_S} \right)^k \geq (1 - \alpha) \left(1 + \frac{t_S}{t_B} \right)^{N_{B,238} + 1} \quad (19.144)$$

2911 First the right-hand side is calculated:

2912
$$(1 - \alpha) \left(1 + \frac{t_S}{t_B} \right)^{N_{B,238} + 1} = (0.95)(2)^{0+1} = 1.90$$

2913 Then, terms of the sum on the left-hand side are accumulated until the total is at least 1.90. The
 2914 iteration stops at $k = 4$, when the sum reaches 1.9375 (illustrated below).

k	k^{th} Term	Sum
0	1	1
1	0.5	1.5
2	0.25	1.75
3	0.125	1.875
4	0.0625	1.9375

2921 Thus, the critical value of the total count is $y_C = 4$, which may also be found in Table G.4 in
 2922 Appendix G. Since the observed count $N_{S,238} = 75$ exceeds the critical count, one concludes that
 2923 the sample contains a positive amount of ^{238}Pu .

2924 The critical net count S_C in this case is also 4, because the blank count is zero. Note that this
 2925 value of S_C is the most conservative of the critical values calculated in this example.

2926 **19E.6 The Minimum Detectable Concentration**

2927 Assume the specified probability of a type II error at the minimum detectable concentration is
 2928 $\beta = 0.05$. The following describes a conservative approach to the estimation of the nominal
 2929 MDC for the analytical process.

2930 Let R_B denote the mean blank count rate for the ^{238}Pu region of interest. Suppose a total of 21
 2931 counts are accumulated in the ^{238}Pu region of interest during ten 60,000-s blank measurements.
 2932 The estimated blank count rate is then

$$2933 \quad R_B = \frac{21}{600,000} = 3.5 \times 10^{-5} \text{ cps}$$

2934 This estimate has a moderately large relative standard uncertainty (approximately 22%), but
 2935 detection decisions are based on the results of shorter measurements (60,000 s, not 600,000 s),
 2936 which will vary even more. So, a conservative upper bound $[N_B]$ will be used for the blank count,
 2937 as suggested in Section 19D.3.2 of Attachment 19D. A method for calculating the critical gross
 2938 count can be adapted to calculate the largest value of the blank count that is likely to be observed
 2939 given the assumption of a mean blank count rate of 3.5×10^{-5} cps. For the current problem, Table
 2940 19.4 will be used, with $R_B t_B$ replacing $R_B t_S$ and $[N_B]$ replacing y_C in the column headings. Since
 2941 the value of $R_B t_B$ is 2.1, which lies between 1.970 and 2.613, Table 19.4 shows that the required
 2942 value is $[N_B] = 5$. Therefore, one expects the number of blank counts observed in 60,000 s (t_B) to
 2943 be no greater than 5. So, the MDC will be calculated here using a critical value $[S_C]$ based on the
 2944 assumption of a blank count $[N_B] = 5$.

2945 The overall sensitivity for the measurement process is the product $A = t_S M_S Y \epsilon R_{238} D_{238}$. Since the
 2946 most variable factor in this product by far is the chemical yield Y , a conservative lower bound for
 2947 A may be found by estimating the β -quantile (5th percentile) of Y and multiplying it by estimated
 2948 values of the other factors. Assume that historical data show that the 5th percentile of Y is approx-
 2949 imately 0.60. Then with the measured efficiency 0.2805, nominal test portion mass 0.5 g, and
 2950 estimated values for the ROI fraction 0.98 and decay factor 0.999, the 5th percentile of A is esti-
 2951 mated as

$$2952 \quad a_\beta = a_{0.05} = (60,000)(0.60)(0.2805)(0.5)(0.98)(0.999) = 4943 \text{ g s}$$

2953 The approximation formulas given in the chapter will be used and the results will be compared to
 2954 the results obtained from a precise power calculation using the value a_β for the sensitivity and
 2955 with the assumptions that the mean blank count rate is $R_B = 3.5 \times 10^{-5}$ cps and that the subsamp-
 2956 ling error is approximately normal.

2957 The following values, which appear in several formulas, are calculated first.

$$c = R_B t_S \left(1 + \frac{t_S}{t_B} \right) = (3.5 \times 10^{-5})(60,000)(1 + 1) = 4.2 \text{ counts}$$

2958

$$I_\beta = 1 - z_{1-\beta}^2 \phi_{\text{Samp}}^2 = 1 - (1.645)^2 (0.05)^2 = 0.993236$$

$$I_\beta c = (0.993236)(4.2) = 4.172 \text{ counts}$$

2959 19E.6.1 Formula A

2960 Assuming the net signal is approximately normal at the MDC, the value of the MDC may be
2961 approximated by

2962

$$x_D = \frac{1}{a_\beta I_\beta} \left([S_C] + \frac{z_{1-\beta}^2}{2} + z_{1-\beta} \sqrt{\frac{z_{1-\beta}^2}{4} + [S_C] + \phi_{\text{Samp}}^2 [S_C]^2 + I_\beta c} \right)$$

2963 where $[S_C]$ denotes the critical net count calculated using $[N_B]$ as the blank count and ϕ_{Samp}^2
2964 denotes the subsampling variance, which also equals $u^2(F_S)$. When Formula A is used, $[S_C]$ is

2965

$$[S_C] = z_{1-\alpha} \sqrt{[N_B] \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B} \right)} = 1.645 \sqrt{(5)(1)(1 + 1)} = 5.201 \text{ counts}$$

2966 and the minimum detectable concentration is

2967

$$x_D = \frac{1}{a_\beta I_\beta} \left([S_C] + \frac{z_{1-\beta}^2}{2} + z_{1-\beta} \sqrt{\frac{z_{1-\beta}^2}{4} + [S_C] + \phi_{\text{Samp}}^2 [S_C]^2 + I_\beta c} \right)$$

$$= \frac{1}{(4943)(0.993236)} \left(5.201 + \frac{1.645^2}{2} + 1.645 \sqrt{\frac{1.645^2}{4} + 5.201 + (0.05)^2 (5.201)^2 + 4.172} \right)$$

$$= 0.0024 \text{ Bq g}^{-1} \quad \text{or} \quad 2.4 \text{ Bq kg}^{-1}$$

2968 If the calculation is repeated with $R_B t_B = 2.1$ substituted for $[N_B] = 5$ as the blank count used to
2969 calculate the critical value, the resulting value of x_D is 1.9 Bq kg^{-1} . A precise power calculation
2970 shows that the actual value of x_D is 2.1 Bq kg^{-1} .

2971 19E.6.2 Formula C

2972 Using Formula C, one obtains

$$\begin{aligned}
 [S_C] &= \frac{z_{1-\alpha}^2 t_S}{2t_B} + z_{1-\alpha} \sqrt{\frac{z_{1-\alpha}^2 t_S^2}{4t_B^2} + [N_B] \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B}\right)} \\
 &= \frac{1.645^2}{2}(1) + 1.645 \sqrt{\frac{1.645^2}{4}(1)^2 + 10} \\
 &= 6.727 \text{ counts}
 \end{aligned}$$

2973 Then the minimum detectable concentration is

$$\begin{aligned}
 x_D &= \frac{1}{a_\beta I_\beta} \left([S_C] + \frac{z_{1-\beta}^2}{2} + z_{1-\beta} \sqrt{\frac{z_{1-\beta}^2}{4} + [S_C] + \Phi_{\text{Samp}}^2 [S_C]^2 + I_\beta c} \right) \\
 &= \frac{1}{(4943)(0.993236)} \left(6.727 + \frac{1.645^2}{2} + 1.645 \sqrt{\frac{1.645^2}{4} + 6.727 + (0.05)^2 (6.727)^2 + 4.172} \right) \\
 &= 0.0028 \text{ Bq g}^{-1} \quad \text{or} \quad 2.8 \text{ Bq kg}^{-1}
 \end{aligned}$$

2975 If the critical value is calculated using $R_b t_B = 2.1$ instead of $[N_B] = 5$, the resulting value of x_D is
 2976 2.3 Bq kg^{-1} . A precise power calculation gives the value $x_D = 2.5 \text{ Bq kg}^{-1}$.

2977 19E.6.3 The Stapleton Approximation

2978 When the Stapleton approximation is used, the critical net count is

$$\begin{aligned}
 [S_C] &= 0.4 \left(\frac{t_S}{t_B} - 1 \right) + \frac{z_{1-\alpha}^2}{4} \left(1 + \frac{t_S}{t_B} \right) + z_{1-\alpha} \sqrt{([N_B] + 0.4) \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B} \right)} \\
 &= 0.4(0) + \frac{1.645^2}{4}(2) + 1.645 \sqrt{(5 + 0.4)(1)(2)} \\
 &= 6.758 \text{ counts}
 \end{aligned}$$

2979 Then the minimum detectable concentration may be approximated by

$$\begin{aligned}
 x_D &= \frac{1}{a_\beta I_\beta} \left([S_C] + \frac{z_{1-\beta}^2}{2} + z_{1-\beta} \sqrt{\frac{z_{1-\beta}^2}{4} + [S_C] + \Phi_{\text{Samp}}^2 [S_C]^2 + I_\beta c} \right) \\
 &= \frac{1}{(4943)(0.993236)} \left(6.758 + \frac{1.645^2}{2} + 1.645 \sqrt{\frac{1.645^2}{4} + 6.758 + (0.05)^2 (6.758)^2 + 4.172} \right) \\
 &= 0.0028 \text{ Bq g}^{-1} \quad \text{or} \quad 2.8 \text{ Bq kg}^{-1}
 \end{aligned}$$

2981 When $R_B t_B$ is substituted for $[N_B]$ in the calculation of the critical value, the resulting value of x_D
 2982 is 2.4 Bq kg⁻¹.

2983 Alternatively, the longer calculation given in Section 19D.3.3 of Attachment 19D may be used.

$$x_D = \frac{1}{a_\beta} \left(\frac{b'^2 - 2a'c' + b' \sqrt{b'^2 - 4a'c'}}{2a'^2} - R_B t_S \right)$$

2985 where

$$a' = 1 - \frac{z_{1-\beta}^2 \Phi_{\text{Samp}}^2}{4} = 0.99831$$

$$b' = 2\sqrt{R_B t_S} + z_{1-\alpha} \sqrt{1 + \frac{t_S}{t_B}} = 5.2244$$

$$c' = R_B t_S + \frac{z_{1-\alpha}^2 - z_{1-\beta}^2}{4} \left(1 + \frac{t_S}{t_B} \right) + z_{1-\alpha} \sqrt{R_B t_S \left(1 + \frac{t_S}{t_B} \right)} = 5.4709$$

2989 Then

$$\begin{aligned}
 x_D &= \frac{5.2244^2 - 2(0.99831)(5.4709) + (5.2244) \sqrt{5.2244^2 - 4(0.99831)(5.4709)}}{2(0.99831)^2 (4943)} - \frac{2.1}{4943} \\
 &= 0.0025 \text{ Bq g}^{-1} \quad \text{or} \quad 2.5 \text{ Bq kg}^{-1}
 \end{aligned}$$

2991 A precise power calculation gives the value $x_D = 2.5 \text{ Bq kg}^{-1}$.

2992 19E.6.4 Exact Test

2993 When the exact test for detection is used, the critical gross count $[y_C]$ equals the smallest nonneg-
 2994 ative integer n such that

2995
$$\sum_{k=0}^n \binom{[N_B] + k}{[N_B]} \left(\frac{t_S}{t_B + t_S} \right)^k \geq (1 - \alpha) \left(1 + \frac{t_S}{t_B} \right)^{[N_B] + 1}$$

2996 The right-hand side of the inequality is found as follows

2997
$$\text{RHS} = (1 - 0.05)(1 + 1)^{5+1} = 60.8$$

2998 The value of the left-hand side exceeds 60.8 when n equals 12

2999
$$\text{LHS} = \binom{5}{5} + \binom{6}{5} \frac{1}{2} + \binom{7}{5} \frac{1}{4} + \dots + \binom{17}{5} \frac{1}{4096} = 60.92$$

3000 Therefore,

3001
$$[y_C] = 12 \text{ counts} \quad \text{and} \quad [S_C] = [y_C] - [N_B] \frac{t_S}{t_B} = 7 \text{ counts}$$

3002 So,

3003
$$\begin{aligned} x_D &= \frac{1}{a_\beta I_\beta} \left([S_C] + \frac{z_{1-\beta}^2}{2} + z_{1-\beta} \sqrt{\frac{z_{1-\beta}^2}{4} + [S_C] + \phi_{\text{Samp}}^2 [S_C]^2 + I_\beta c} \right) \\ &= \frac{1}{(4943)(0.993236)} \left(7 + \frac{1.645^2}{2} + 1.645 \sqrt{\frac{1.645^2}{4} + 7 + (0.05)^2 (7)^2 + 4.172} \right) \\ &= 0.0029 \text{ Bq g}^{-1} \quad \text{or} \quad 2.9 \text{ Bq kg}^{-1} \end{aligned}$$

3004 The result of the precise calculation is $x_D = 2.8 \text{ Bq kg}^{-1}$.

3005 **19E.7 The Minimum Quantifiable Concentration**

3006 For the purpose of this example, the MQC is defined to be the analyte concentration x_Q at which
 3007 the relative standard deviation of the measured result is $1/k_Q$, where $k_Q = 10$. Calculation of x_Q
 3008 requires knowledge of the relative standard deviation of the measured sensitivity when the true
 3009 sensitivity is $A = a_{0.05}$. Assume for this example that the relative standard deviation is $\phi_{\hat{A}} \approx 0.051$
 3010 (5.1%) at $A = a_{0.05} = 4943$. Then

$$x_Q = \frac{k_Q^2}{2a_{0.05}I_Q} \left(1 + \sqrt{1 + \frac{4I_Q R_B t_S}{k_Q^2} \left(1 + \frac{t_S}{t_B} \right)} \right)$$

3011 where

$$I_Q = 1 - k_Q^2(\phi_{\hat{A}}^2 + \phi_{\text{Samp}}^2) = 1 - 10^2(0.051^2 + 0.05^2) = 0.4899$$

3012 Then

$$\begin{aligned} x_Q &= \frac{10^2}{2(4943)(0.4899)} \left(1 + \sqrt{1 + \frac{4(0.4899)(3.5 \times 10^{-5})(60,000)}{10^2} (1 + 1)} \right) \\ &= 0.042 \text{ Bq g}^{-1} \quad \text{or} \quad 42 \text{ Bq kg}^{-1} \end{aligned}$$

3013 The MQC is substantially increased by the measurement variance of the sensitivity \hat{A} and the
 3014 subsampling variance. Without them the minimum quantifiable concentration would be only
 3015 21 Bq kg⁻¹. Note also that if either the relative standard deviation of \hat{A} or the subsampling stan-
 3016 dard deviation were 0.1 or more, the MQC would be infinite.

ATTACHMENT 19F
Tests for Normality

3017
3018

3019 **19F.1 Purpose**

3020 Many common statistical hypothesis tests are based on the assumption that data are normally dis-
3021 tributed. Normality is often assumed by default, but, since some tests may not perform well with
3022 data that are not normal, it is often important to check the validity of the assumption. Performing
3023 a test for normality cannot prove that data are normally distributed, but it may produce strong
3024 evidence that they are not.

3025 There are a number of tests for normality. Each test requires a random sample Y_1, Y_2, \dots, Y_n from
3026 the distribution being checked. Whatever test is used, it is a good idea to plot the data for visual
3027 inspection. The normal probability plot described in Section 19F.2 is useful for this purpose.

3028 One of the most powerful tests for normality is the Shapiro-Wilk test, but it is difficult to imple-
3029 ment manually. EPA QA/G-9 recommends the Shapiro-Wilk test when the sample size n is less
3030 than 50, and either Filliben's statistic or the studentized range test when $n > 50$ (EPA 1998). In
3031 fact, if software for the Shapiro-Wilk test is not available, then Filliben's statistic may be used in
3032 all cases for which critical values are available. Instructions for computing and using Filliben's
3033 statistic are given in Section 19F.3.

3034 **19F.2 Normal Probability Plots**

3035 A normal probability plot is a graph of the observed quantiles of a data set against the correspon-
3036 ding quantiles of a standard normal distribution. If the data are normally distributed and the data
3037 set is large enough (more than about 10 values), the plotted points should lie approximately on a
3038 straight line. A preliminary decision about the distribution of the data may be based on inspection
3039 of the graph. Normal probability plots may be produced manually, although software is generally
3040 needed to make plots of large data sets feasible.

3041 Manual construction of a normal probability plot is easier when pre-printed normal probability
3042 paper is available (see Figure 19.18 at the end of this attachment).

3043 To plot a set of data on normal probability paper, perform the following steps (EPA 1998).

3044 1. Arrange the data in ascending order:

3045
$$Y_{(1)} \leq Y_{(2)} \leq \dots \leq Y_{(n)}$$

- 3046 2. Label the vertical axis to encompass all values between $Y_{(1)}$ (the minimum) and $Y_{(n)}$ (the
3047 maximum).
- 3048 3. For each i compute the cumulative frequency F_i of the value $Y_{(i)}$, which is defined as the
3049 number of values in the data set that are less than or equal to $Y_{(i)}$. (Note that $F_i \geq i$.)
- 3050 4. Compute the horizontal coordinate $X_i = F_i / (n + 1) \times 100\%$ for each i .
- 3051 5. Plot each ordered pair $(X_i, Y_{(i)})$ at the appropriate location on the grid.

3052 To plot a set of data on ordinary graph paper, perform Steps 1–3 above followed by Steps 4'–6'
3053 below.

- 3054 4'. For each i , determine the quantile $X_i = z_{F_i/(n+1)}$ of the standard normal distribution (see
3055 for example Table G.1).
- 3056 5'. Label the horizontal axis to encompass all values between X_1 and X_n .
- 3057 6'. Plot each ordered pair $(X_i, Y_{(i)})$.

3058 The latter version of the procedure can be adapted to construct probability plots for other types of
3059 distributions. Only Step 4' must change, since X_i is required to be a quantile of the appropriate
3060 distribution.

EXAMPLE	
3061	
3062	Problem: Given the data set
3063	123 122 124 118 118 122 121 117 125 119
3064	construct a normal probability plot using normal probability paper.
3065	Solution:
3066	Step 1 Sort the 10 values:
	117 118 118 119 121 122 122 123 124 125
3067	Step 2 Label the vertical axis to encompass the values from 117 to 125.

3068 Step 3 For each i compute the cumulative frequency F_i of $Y_{(i)}$ (see the table below).

3069 Step 4 For each i compute $X_i = (F_i / 11) \times 100\%$ and plot $(X_i, Y_{(i)})$.

i	1	2	3	4	5	6	7	8	9	10
$Y_{(i)}$	117	118	118	119	121	122	122	123	124	125
F_i	1	3	3	4	5	7	7	8	9	10
X_i	9.1%	27.3%	27.3%	36.4%	45.5%	63.6%	63.6%	72.7%	81.8%	90.9%

The results are shown as a normal probability plot in Figure 19.18.

3070 **19F.3 Filliben’s Statistic**

3071 Filliben’s statistic is derived from the concept of the normal probability plot and is often called
 3072 the “normal probability plot correlation coefficient.” The use of the statistic makes the
 3073 interpretation of the probability plot less subjective, although a visual inspection of the plot is
 3074 still recommended. The procedure for calculating and using the statistic is given below (Filliben
 3075 1975).

3076 1. Choose the significance level α .

3077 2. Arrange the data in ascending order.

3078
$$Y_{(1)} \leq Y_{(2)} \leq \dots \leq Y_{(n)}$$

3079 3. Compute the quantities \bar{Y} and S as follows.

3080
$$\bar{Y} = \frac{1}{n} \sum_{i=1}^n Y_i \qquad S = \sqrt{\sum_{i=1}^n (Y_i - \bar{Y})^2}$$

3081 4. For $i = 1, 2, \dots, n$, compute

3082
$$m_i = \begin{cases} 1 - 0.5^{1/n}, & i = 1 \\ (i - 0.3175) / (n + 0.365), & i = 2, 3, \dots, n - 1 \\ 0.5^{1/n}, & i = n \end{cases}$$

3083 and let M_i be the m_i -quantile of the standard normal distribution z_{m_i} . (Table G.1 in
3084 Appendix G may be interpolated to obtain approximate values of these quantiles.)

3085 5. Compute $c_n = \sqrt{\sum_{i=1}^n M_i^2}$.

3086 6. Compute Filliben's statistic r (the normal probability plot correlation coefficient).

3087
$$r = \frac{\sum_{i=1}^n Y_{(i)} M_i}{c_n S}$$

3088 7. Determine a critical value from Table G.5. If r is less than the critical value, conclude that
3089 the data are not normally distributed.

3090

EXAMPLE

3091

Problem: Determine whether the values

3092

123 122 124 118 118 122 121 117 125 119

3093

appear to come from a normal distribution. Use the significance level 0.05.

3094

Solution:

3095

Step 1 The significance level is specified to be $\alpha = 0.05$.

3096

Step 2 Sort the 10 values:

117 118 118 119 121 122 122 123 124 125

3097 Step 3 Compute $\bar{Y} = \frac{1}{10} \sum Y_i = 120.9$ and

$$S = \sqrt{\sum (Y_i - 120.9)^2} = 8.301$$

3098 Step 4 For each i compute m_i and $M_i = z_{m_i}$ (see the table below). (The quantiles M_i in this example have been computed without using Table G.1.)

3099 Step 5 Compute $c_n = \sqrt{\sum_{i=1}^{10} M_i^2} = \sqrt{7.575} = 2.752$.

3100 Step 6 Compute $r = \frac{\sum_{i=1}^{10} Y_{(i)} M_i}{c_n S} = \frac{22.37}{(2.752)(8.301)} = 0.979$.

3101 Step 7 Table G.5 shows that the critical value for $n = 10$ and $\alpha = 0.05$ is 0.917. Since $0.979 \geq 0.917$, the data appear to be normally distributed.

i	1	2	3	4	5	6	7	8	9	10
$Y_{(i)}$	117	118	118	119	121	122	122	123	124	125
m_i	0.06697	0.1623	0.2588	0.3553	0.4518	0.5482	0.6447	0.7412	0.8377	0.9330
M_i	-1.499	-0.9849	-0.6470	-0.3711	-0.1212	0.1212	0.3711	0.6470	0.9849	1.499

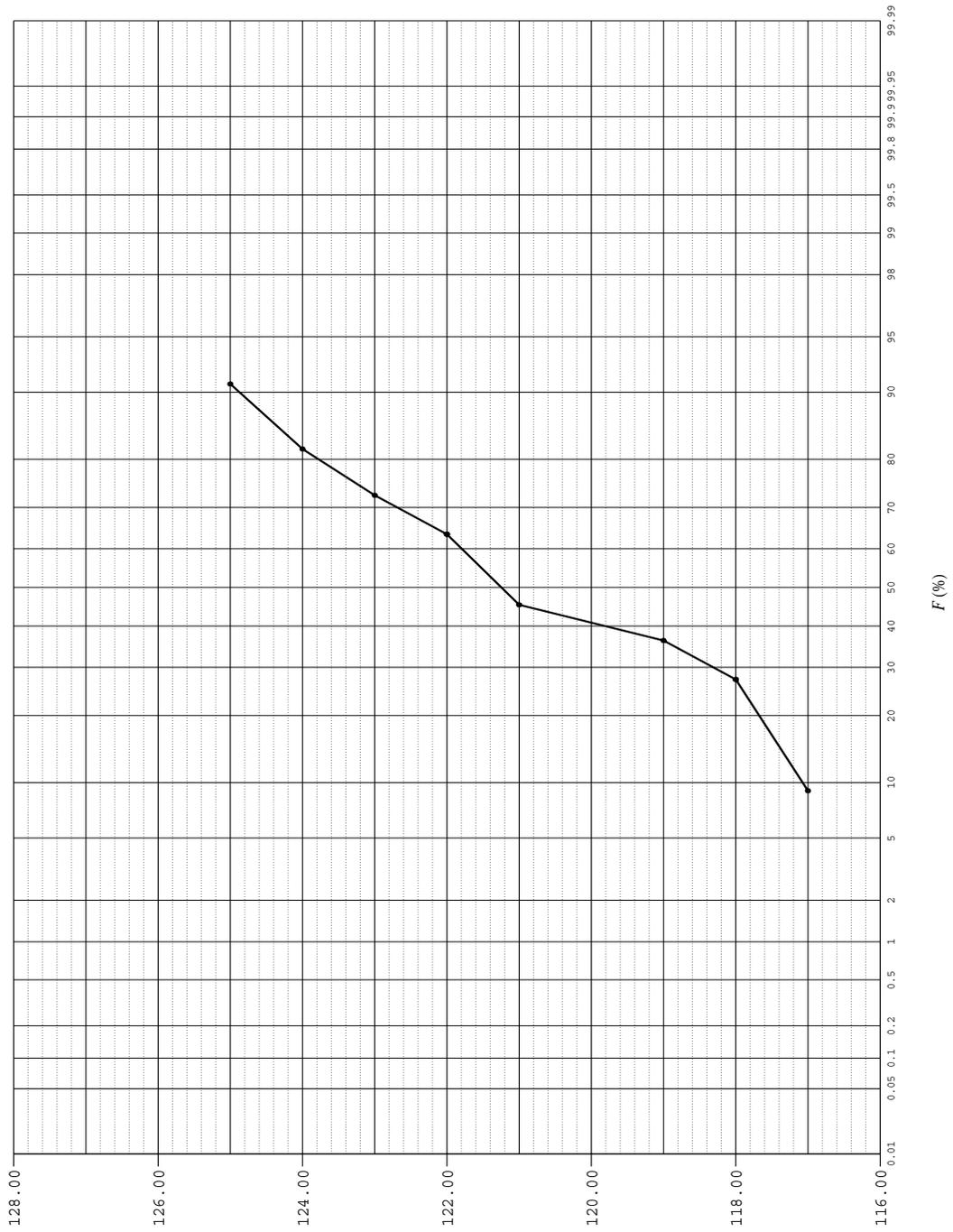


FIGURE 19.18 — Example: Normal probability plot

3102 **19F.4 References**

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3104 *Practical Methods for Data Analysis*. EPA QA/G-9, QA97 Version. EPA/600/R-96/084,
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3108
3109

ATTACHMENT 19G Balance Measurement Uncertainty

3110

19G.1 Purpose

3111 This attachment describes methods that may be used to evaluate balance measurement uncer-
3112 tainty. The relative standard uncertainty of a measurement made with a laboratory balance tends
3113 to be small if the balance is used properly, and it may even be considered negligible when com-
3114 pared to other uncertainties associated with radioanalysis (e.g., see Section 19.6.11, “Subsamp-
3115 ling”). However, one needs to know the performance limits of any measuring instrument. For
3116 example, the measurement uncertainty may actually be relatively large if a balance is used to
3117 weigh a mass that is too small for it. Establishing reasonable acceptance criteria for balance qual-
3118 ity control also requires an understanding of the sources of the measurement uncertainty.

3119

19G.2 Considerations

3120 Regardless of the methods used to evaluate balance measurement uncertainty, the results may be
3121 misleading unless the balance is well maintained and protected from external influences, such as
3122 drafts and sudden changes in pressure, temperature and humidity.

3123 The appropriate method for evaluating the standard uncertainty of a mass measured using a bal-
3124 ance depends on the type of balance, including its principles of calibration and operation, but the
3125 uncertainty of the measured result generally has components associated with balance sensitivity,
3126 linearity, repeatability, and air buoyancy. Typically, the component associated with sensitivity
3127 includes the uncertainty of calibration and may include variability caused by changing environ-
3128 mental conditions, such as temperature. Other sources of uncertainty may include leveling errors
3129 and off-center errors, which should be controlled. Static electrical charges may also have an
3130 effect. Changes in mass (e.g., by absorption or evaporation of water) may be very significant for
3131 some materials.

3132

19G.3 Repeatability

3133 The repeatability of a balance is expressed as a standard deviation and is usually assumed to be
3134 independent of the load. It represents the variability of the result of zeroing the balance, loading a
3135 mass on the pan, and reading the indication.

3136 Balance manufacturers provide specifications for repeatability, but a test of repeatability should
3137 also be part of the routine quality control for the balance (see ASTM 1993). The simplest pro-
3138 cedure for evaluating repeatability is to make a series of replicate measurements of a mass

3139 standard under “repeatability conditions.” Repeatability conditions require one balance, one
 3140 observer, one measurement location, and repetition during a short time period. For each
 3141 measurement, one must zero the balance, load the mass standard, and read the balance indication.

3142 A nested experimental design can also be used to evaluate both the repeatability and the day-to-
 3143 day variability due to environmental factors. In this procedure, one makes a series of replicate
 3144 measurements with the same mass standard each day for a number of days. Ideally one should
 3145 use a mass near the capacity of the balance to obtain the most reliable estimate of day-to-day var-
 3146 iability. The repeatability standard deviation is then estimated by

$$s_r = \sqrt{\frac{1}{K(J-1)} \sum_{k=1}^K \sum_{j=1}^J (x_{k,j} - \bar{x}_k)^2} \quad (19.150)$$

3147 where

- 3148 s_r is the estimated repeatability standard deviation
- 3149 J is the number of repetitions per day
- 3150 K is the number of days
- 3151 $x_{k,j}$ is the j^{th} result obtained on the k^{th} day
- 3152 \bar{x}_k is the average of all the results on the k^{th} day

3153 The repeatability standard deviation determined by this method is a Type A standard uncertainty
 3154 with $K(J - 1)$ degrees of freedom.

3155 19G.4 Environmental Factors

3156 Given the experimental data from the preceding section, one may estimate the variability due to
 3157 environmental factors (day-to-day variability) as follows.²⁹

$$s_{\text{Env}}^2 = \frac{1}{K-1} \sum_{k=1}^K (\bar{x}_k - \bar{\bar{x}})^2 - \frac{s_r^2}{J} \quad (19.151)$$

3158 where

- 3159 s_{Env}^2 is the estimated variance due to environmental factors
- 3160 $\bar{\bar{x}}$ is the grand average of all the data (the average of the \bar{x}_k)

²⁹ 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 $J s_{\bar{x}}^2 / s_r^2$, 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.

3161 If s_{Env}^2 is found to be positive, then s_{Env} is estimated by its square root; otherwise, s_{Env} is assumed
 3162 to be zero. One estimates the relative component of standard uncertainty of a measured mass due
 3163 to environmental factors by

$$\varphi_{\text{Env}} = \frac{s_{\text{Env}}}{M_{\text{Check}}} \quad (19.152)$$

3164 where M_{Check} is the mass of the standard used in the experiment.

3165 **19G.5 Calibration**

3166 The uncertainty of calibration includes components associated with the mass standard or stan-
 3167 dards, repeatability, and variability due to environmental factors.

3168 When a precision mass standard is used for calibration, the standard uncertainty of its mass is
 3169 generally negligible. However, the uncertainty may be evaluated if necessary from the specified
 3170 mass tolerance. For example, a 100-g ASTM Class-1 mass standard has a tolerance of 0.00025 g,
 3171 which may be assumed to represent the half-width of a triangular distribution centered at zero
 3172 (ASTM 1991). The standard uncertainty may be found by dividing this tolerance by $\sqrt{6}$ and is
 3173 approximately 0.00010 g, or 1.0×10^{-6} when expressed in relative terms.

3174 The total relative standard uncertainty of a measured mass due to calibration may be estimated as
 3175 follows.

$$\varphi_{\text{Cal}} = \sqrt{\varphi_{\text{Env}}^2 + \frac{s_r^2 + a_{\text{Cal}}^2 / 6}{M_{\text{Cal}}^2}} \quad (19.153)$$

3176 where

3177 φ_{Cal} is the total relative standard uncertainty of a balance measurement due to calibration
 3178 φ_{Env} is the relative standard uncertainty due to environmental factors
 3179 s_r is the repeatability standard deviation
 3180 a_{Cal} is the tolerance for the mass of the calibration standard
 3181 M_{Cal} is the mass of the standard used for calibration

3182 If environmental conditions are not well-controlled, φ_{Env} may tend to dominate the other compo-
 3183 nents here, since both s_r and a_{Cal} are much smaller than M_{Cal} .

3184 **19G.6 Linearity**

3185 The linearity of a balance should be specified by the manufacturer as a tolerance, a_L , which repre-
 3186 sents the maximum deviation of the balance indication from the value that would be obtained by
 3187 linear interpolation between the calibration points. Routine quality control should ensure that the
 3188 linearity remains within acceptable limits.

3189 The *Eurachem/CITAC Guide: Quantifying Uncertainty in Analytical Measurement* recommends
 3190 that the linearity tolerance a_L be treated as the half-width of a rectangular distribution and that a_L
 3191 therefore be divided by $\sqrt{3}$ to obtain the standard uncertainty (Eurachem 2000). However, since
 3192 the linearity error is likely to vary as a sinusoidal function of the load, the divisor $\sqrt{2}$ may be
 3193 more appropriate. So, the standard uncertainty due to linearity for a simple mass measurement
 3194 may be evaluated as $a_L / \sqrt{2}$. Whether one uses $\sqrt{3}$ or the more conservative value $\sqrt{2}$ depends
 3195 partly on how conservative one believes the estimate of a_L to be.

3196 **19G.7 Air Buoyancy Corrections**

3197 Air buoyancy corrections have not often been performed in radiochemistry laboratories, but they
 3198 are necessary for a realistic estimate of the standard uncertainty of a mass measurement,
 3199 especially when the material being weighed has a low density. Failure to correct for air buoyancy
 3200 when weighing water, for example, introduces a relative error of approximately -0.1%, which
 3201 may be much larger than the standard uncertainty of the uncorrected mass (e.g., when weighing a
 3202 gram or more of an aqueous solution on a typical four-place analytical balance).

3203 When a buoyancy correction factor is used, the true mass is estimated as follows.

$$m = I_{\text{Net}} B \quad (19.154)$$

3204 where

$$B = \frac{1 - \rho_{A,C} / \rho_C}{1 - \rho_{A,M} / \rho_M} \quad (19.155)$$

3205 and

- 3206 m is the corrected value for the mass of the material being weighed
- 3207 I_{Net} is the net balance indication
- 3208 B is the buoyancy correction factor
- 3209 ρ_M is the density of the material being weighed
- 3210 $\rho_{A,M}$ is the density of the air at the time the material is weighed

3211 ρ_C is the density of the calibration mass standard
 3212 $\rho_{A,C}$ is the density of the air at the time of calibration

3213 The standard uncertainty of B may be obtained as follows.

$$\frac{u^2(B)}{B^2} = \frac{\frac{u^2(\rho_{A,C})}{\rho_{A,C}^2} - 2\frac{u(\rho_{A,C}, \rho_C)}{\rho_{A,C}\rho_C} + \frac{u^2(\rho_C)}{\rho_C^2}}{\left(\frac{\rho_C}{\rho_{A,C}} - 1\right)^2} + \frac{\frac{u^2(\rho_{A,M})}{\rho_{A,M}^2} - 2\frac{u(\rho_{A,M}, \rho_M)}{\rho_{A,M}\rho_M} + \frac{u^2(\rho_M)}{\rho_M^2}}{\left(\frac{\rho_M}{\rho_{A,M}} - 1\right)^2} \quad (19.156)$$

3214 Evaluation of this uncertainty requires estimates of ρ_M , ρ_C , $\rho_{A,M}$ and $\rho_{A,C}$ as well as their standard
 3215 uncertainties and covariances. The covariance $u(\rho_{A,C}, \rho_C)$ is usually zero or negligible, and
 3216 $u(\rho_{A,M}, \rho_M)$ also is usually negligible if the material being weighed is a solid.

3217 The density of air at any time (ρ_A) depends on temperature, pressure, and humidity, as shown in
 3218 the following equation.

$$\rho_A = \rho_0 \left(\frac{273.15}{273.15 + T} \right) \left(\frac{P - (0.3783)(RH / 100\%)(P_{\text{vap}})}{760} \right) \quad (19.157)$$

3219 where

3220 ρ_A is the density of air
 3221 ρ_0 is the density of dry air at 0°C and 760 torr (mm of Hg)
 3222 T is the temperature (°C)
 3223 P is the barometric pressure (torr)
 3224 RH is the relative humidity (%)
 3225 P_{vap} is the vapor pressure (torr) of water at temperature T

3226 The vapor pressure, P_{vap} , is a nonlinear function of T , but it can be approximated by a linear
 3227 function in the range of temperatures typically encountered in the laboratory. When this approxi-
 3228 mation is made, the resulting equation for the air density (g mL^{-1}) may be written as follows.

$$\rho_A = \frac{aP - (RH)(bT - c)}{273.15 + T} \quad (19.158)$$

3229 where

Measurement Statistics

3230 $a = 4.64746 \times 10^{-4}$
3231 $b = 2.5211151 \times 10^{-6}$
3232 $c = 2.0590571 \times 10^{-5}$

3233 Then the standard uncertainty of ρ_A is given by

$$u(\rho_A) = \frac{\sqrt{a^2 u^2(P) + (bRH + \rho_A)^2 u^2(T) + (bT - c)^2 u^2(RH)}}{273.15 + T} \quad (19.159)$$

3234 The density of the calibration weight (ρ_C) and of the solid or liquid material being weighed (ρ_M)
3235 also depend on temperature somewhat, but these temperature effects can usually be safely
3236 ignored when calculating the uncertainty of the buoyancy correction factor, since temperature
3237 affects the density of air much more than the density of a solid or liquid.

3238 The effect of pressure on the density of the material being weighed can also usually be neglected.
3239 For most practical purposes, the compressibility of a solid or liquid can be considered to be zero.

3240

EXAMPLE

3241 Suppose the density of the weighed material, ρ_M , is 0.5 g mL^{-1} with a tolerance of 0.2 g mL^{-1} ,
3242 assumed to represent the half-width of a triangular distribution. The density of the calibration
3243 mass standard, ρ_C , is 7.850 g mL^{-1} with a tolerance of 0.025 g mL^{-1} . Instead of measuring tem-
3244 perature, pressure and humidity at the time of each measurement, the laboratory assumes the
3245 following nominal values and tolerances:

3246	Temperature	22.5	± 4	$^{\circ}\text{C}$
3247	Pressure	750	± 20	torr
3248	Relative humidity	50	± 20	%

3249 Then

$$\begin{aligned} \rho_{A,C} = \rho_{A,M} &= \frac{aP - (\text{RH})(bT - c)}{273.15 + T} \\ &= \frac{(4.64746 \times 10^{-4})(750) - (50)((2.5211151 \times 10^{-6})(22.5) - 2.0590571 \times 10^{-5})}{273.15 + 22.5} \\ &= 1.1728 \times 10^{-3} \text{ g mL}^{-1} \end{aligned}$$

3251 If each of the tolerances for T , P , and RH represents the half-width of a rectangular
3252 distribution, then

$$3253 \quad u^2(T) = \frac{4^2}{3} = \frac{16}{3}, \quad u^2(P) = \frac{20^2}{3} = \frac{400}{3}, \quad \text{and} \quad u^2(\text{RH}) = \frac{20^2}{3} = \frac{400}{3}$$

3254 So, the standard uncertainties of $\rho_{A,C}$ and $\rho_{A,M}$ are

$$\begin{aligned} u(\rho_{A,C}) = u(\rho_{A,M}) &= \frac{\sqrt{a^2 u^2(P) + (b\text{RH} + \rho_A)^2 u^2(T) + (bT - c)^2 u^2(\text{RH})}}{273.15 + T} \\ &= \frac{\sqrt{a^2(400/3) + (b(50) + 1.1728 \times 10^{-3})^2(16/3) + (b(22.5) - c)^2(400/3)}}{273.15 + 22.5} \\ &= 2.1 \times 10^{-5} \text{ g mL}^{-1} \end{aligned}$$

3256 Then the buoyancy correction factor is

$$3257 \quad B = \frac{1 - \rho_{A,C} / \rho_C}{1 - \rho_{A,M} / \rho_M} = \frac{1 - 1.1728 \times 10^{-3} / 7.85}{1 - 1.1728 \times 10^{-3} / 0.5} = 1.00220$$

3258 The tolerances for the densities ρ_C and ρ_M are the half-widths of triangular distributions; so,

$$3259 \quad u^2(\rho_C) = \frac{0.25^2}{6} \quad \text{and} \quad u^2(\rho_M) = \frac{0.2^2}{6}$$

3260 The covariances $u(\rho_{A,C}, \rho_C)$ and $u(\rho_{A,M}, \rho_M)$ are zero in this example. So, the standard uncer-
 3261 tainty of B is

$$u(B) = B \sqrt{\frac{u^2(\rho_{A,C}) / \rho_{A,C}^2 + u^2(\rho_C) / \rho_C^2}{(\rho_C / \rho_{A,C} - 1)^2} + \frac{u^2(\rho_{A,M}) / \rho_{A,M}^2 + u^2(\rho_M) / \rho_M^2}{(\rho_M / \rho_{A,M} - 1)^2}}$$

$$= 1.00220 \sqrt{\frac{\frac{(2.1 \times 10^{-5})^2}{(1.1728 \times 10^{-3})^2} + \frac{0.25^2}{6 \cdot 7.85^2}}{\left(\frac{7.85}{1.1728 \times 10^{-3}} - 1\right)^2} + \frac{\frac{(2.1 \times 10^{-5})^2}{(1.1728 \times 10^{-3})^2} + \frac{0.2^2}{6 \cdot 0.5^2}}{\left(\frac{0.5}{1.1728 \times 10^{-3}} - 1\right)^2}}$$

$$= 3.87 \times 10^{-4}$$

3263 Thus, the buoyancy correction factor increases the result of the measurement by 0.22% and
 3264 generates an uncertainty component of approximately 0.04%. Note that this uncertainty
 3265 component is very small and would generally be considered negligible in the final result of a
 3266 radiochemistry measurement, but it may represent a significant fraction of the uncertainty of
 3267 the mass measurement.

19G.8 Combining the Components

3269 When the balance is used to measure the mass, m , of an object placed on the pan, the mass is
 3270 given by $m = IB$, and its standard uncertainty by

$$u(m) = \sqrt{B^2 \left(I^2 (\varphi_{\text{Cal}}^2 + \varphi_{\text{Env}}^2) + \frac{a_L^2}{2} + s_r^2 \right) + I^2 u^2(B)} \quad (19.160)$$

3271 where

- 3272 m is the buoyancy-corrected mass
- 3273 I is the balance indication
- 3274 B is the buoyancy correction factor
- 3275 φ_{Cal} is the relative standard uncertainty due to calibration
- 3276 φ_{Env} is the relative standard uncertainty due to environmental factors
- 3277 a_L is the linearity tolerance
- 3278 s_r is the repeatability standard deviation

3279 Often the balance is used to weigh material in a container. The balance is zeroed with the empty
 3280 container on the pan and the container is then filled and weighed without being removed from the
 3281 pan. In this case the linearity uncertainty component is counted twice, because the linearity error
 3282 is assumed to vary between the two loads. (This assumption tends to be conservative when small
 3283 masses are weighed.) Although the buoyancy factor for the tare and gross measurements may be
 3284 different because of the different densities of the container and the material inside it, the only
 3285 value of B that is used is the buoyancy factor for the material being weighed.

3286 In a third scenario, the empty container is weighed, removed from the pan, and then filled with
 3287 material. The balance is zeroed again, and the filled container is weighed. Finally, the net mass is
 3288 determined by subtracting the mass of the empty container from the total mass of the container
 3289 and material. In this case both the linearity and repeatability components of uncertainty must be
 3290 counted twice, because two distinct measurements are made. So, the corrected net mass and its
 3291 standard uncertainty are

$$m = I_{\text{Net}} B$$

$$u(m) = \sqrt{B^2 (I_{\text{Net}}^2 (\phi_{\text{Cal}}^2 + \phi_{\text{Env}}^2) + a_L^2 + 2s_r^2) + I_{\text{Net}}^2 u^2(B)} \quad (19.161)$$

3292 where

3293 I_{Net} is the net balance indication (Gross - Tare)
 3294 B is the buoyancy factor for the material being weighed

3295 19G.9 References

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