

7020 QUALITY SYSTEM*

7020 A. Quality Systems/Quality Assurance/Quality Control Program

1. Introduction

Every laboratory that analyzes environmental water and wastewater samples for radionuclides should operate under a quality system, which establishes the basis for all of the laboratory's quality assurance (QA) and quality control (QC) activities. The quality system sets forth requirements for the laboratory's organizational framework, the structure and contents of its quality manual, document controls, method validation, QC of measurement processes, internal audits, documentation, and completed-record archives. Quality system standards commonly implemented at laboratories include the National Environmental Laboratory Accreditation Conference (NELAC) Institute (TNI) Standard^{1†} and *General Requirements for the Competence of Testing and Calibration Laboratories* (ISO 17025).² *The Manual for the Certification of Laboratories Analyzing Drinking Water—Criteria and Procedures, Quality Assurance*³ also addresses QA and QC requirements established by the U.S. Environmental Protection Agency (EPA) for Safe Drinking Water Act compliance testing.

The laboratory's quality manual may include the laboratory's standard operating procedures (SOPs) by reference. It also addresses default QC measures applicable to instrument calibration and performance checks, background measurements, and batch QCs for precision and bias (accuracy) of analytical measurements. Also essential is a manual of analytical methods (or at least copies of approved methods).

Analysts must be trained in accordance with the quality manual and be familiar with its contents and requirements. The quality manual must also be readily accessible to them as they work in the laboratory.

2. QC Program Performance Criteria

Successful QC programs define acceptable, attainable performance criteria for precision and bias. These criteria must both reflect the laboratory's capabilities and be applicable to the programs for which analysis is performed.

Initially, performance criteria can be drawn up based on data derived from initial use of the analytical method at the laboratory. Performance criteria may also be based on criteria set by the party requiring the water analyses (e.g., regulators). Such criteria should be analysis-specific and may vary by project. For example, NELAC has compiled allowable deviations for Safe Drinking Water Act compliance monitoring samples (see Table 7020:I). The laboratory may use published values until enough data can be compiled to set experience-based criteria that reflect actual method performance as it is performed at the laboratory.

3. Minimum QC Program

Each laboratory should establish and implement QC requirements that are consistent with the data quality objectives (DQOs) and measurement quality objectives (MQOs)[‡] of the programs they support. At minimum, the laboratory's QC program should include a number of integrated QC measures that address basic instrument performance, initial and ongoing calibrations, background measurement stability, and the precision and bias (accuracy) of each method (as measured via batch QC samples).

Typical batch QCs include negative controls (e.g., reagent or method blanks); positive controls [e.g., laboratory-fortified blanks (LFB), laboratory control samples (LCS), and matrix spikes (MS)]; reproducibility controls (e.g., sample and matrix-spiked duplicates); sample-specific controls (acceptable range for tracer or carrier chemical yield, criteria for spectral resolution, agreement between peaks' observed energy and accepted values, etc.); and instrument controls (e.g., controls on background subtraction count determinations, instrument performance checks, calibration verifications). Such QCs can be monitored via statistical QC and tolerance charts. Certain aspects of radiochemical instrument and background QCs are instrument- or method-specific; these are dealt with in the individual methods and should be addressed in the laboratory's quality manual.

Prepare instrument QC charts^{4,5,6} by plotting a reference source's counts on a graph in which the abscissa is time and the ordinate is count rate, total counts, or another appropriate parameter. Determine the "true" (mean) value by averaging the results of at least 20 measurements with acceptable individual statistics. Insert lines parallel to the time axis at the mean value and the values for ± 2 and ± 3 standard deviations. These lines should include appropriate corrections for decay of the radionuclide of interest.

Sometimes the statistically determined performance may be better than required to maintain control based on applicable DQOs and MQOs; if so, tolerance limits may be established as the control criterion. On the control chart, draw lines indicating the tolerance limits for the method's specified performance requirements, along with lines indicating its statistical performance (i.e., ± 3 standard deviations). As long as the method's statistical performance falls within the tolerance limit, the tolerance chart will supply evidence that the measurement parameter in question is under control.

Interpret the QC chart data objectively. When a point goes outside established limits, determine whether the excursion is a random occurrence by repeating the measurement or by running repeated measurements and applying statistical tests (e.g., a Chi-square test) to determine whether the variation was non-statistical.

* Reviewed by Standard Methods Committee, 2011.

Joint Task Group: Robert T. Shannon

† At press time, implementation of the 2009 version of the TNI standard was underway.

‡ See MARLAP⁴ for definition and complete discussion of the concept and use of Measurement Quality Objectives.

QUALITY SYSTEM (7020)/Quality Systems/Quality Assurance/Quality Control Program

TABLE 7020:I. LABORATORY PRECISION—ONE STANDARD DEVIATION VALUES FOR VARIOUS ANALYSES IN SAFE DRINKING WATER COMPLIANCE SAMPLES*

Analyte	Spike Level (μ †) Range	Expected Mean	Acceptable Standard Deviation (σ_{NELAC})
Gross Alpha	7 to 75 pCi/L	$0.8586\mu + 1.4802$	$0.1610\mu + 1.1366$
Gross Beta	8 to 75 pCi/L	$0.8508\mu + 2.9725$	$0.0571\mu + 2.9372$
Barium-133	10 to 100 pCi/L	$0.9684\mu + 0.1424$	$0.0503\mu + 1.0737$
Cesium-134	10 to 100 pCi/L	$0.9369\mu + 0.0845$	$0.0482\mu + 0.9306$
Cesium-137	20 to 240 pCi/L	$1.0225\mu + 0.2624$	$0.0347\mu + 1.5185$
Cobalt-60	10 to 120 pCi/L	$1.0257\mu + 0.3051$	$0.0335\mu + 1.3315$
Iodine-131	3 to 30 pCi/L	$0.9711\mu + 0.8870$	$0.0624\mu + 0.6455$
Radium-226	1 to 20 pCi/L	$0.9253\mu + 0.3175$	$0.0942\mu + 0.0988$
Radium-228	2 to 20 pCi/L	$0.9243\mu + 0.2265$	$0.1105\mu + 0.3788$
Strontium-89	10 to 70 pCi/L	$0.9648\mu + 0.1591$	$0.0379\mu + 2.6203$
Strontium-90	3 to 45 pCi/L	$0.9369\mu + 0.2279$	$0.0902\mu + 0.5390$
Tritium	1000 to 24 000 pCi/L	$0.9883\mu + 46.4776$	$0.0532\mu + 38.8382$
Natural uranium (activity)	2 to 70 pCi/L	$0.9568\mu + 0.0773$	$0.0700\mu + 0.2490$
Uranium (mass)	3 to 104 $\mu\text{g/L}$	$0.9568\mu + 0.1153$	$0.0700\mu + 0.3700$
Zinc-65	30 to 360 pCi/L	$1.0495\mu + 0.1245$	$0.0530\mu + 1.8271$

* Modified from: NELAC PT for Accreditation Fields of Proficiency Testing with PTRs, Drinking Water. Effective October 1, 2007, NELAC_DW_RAD_FOFT_Eff_2007_10_01-2.xls, available at: <http://www.nelac-institute.org/foft.php>. Accessed August 2011.

† Acceptable limits are $\mu \pm 3\sigma$; warning limits are $\mu \pm 2\sigma$.

Control charts may indicate trends. For example, if regular measurements of the check source show a movement in one direction, one can infer that some system variable is changing. The change may or may not need to be corrected, but it should trigger an investigation and, when needed, corrective actions that will ensure subsequent analyses produce data that meet applicable DQOs and MQOs.

When QC charts indicate that instrument performance has changed significantly, corrective actions (ranging from data inspection to instrument maintenance and recalibration) should be made. Trends in QC charts may warn of an impending need for corrective actions. Trending criteria should be as simple as possible but result in meaningful control of the related parameter. For example, multiple successive points less than 1 standard deviation on one side of the mean may not require action when the analysis is not negatively affected. The laboratory's quality manual should unambiguously specify all trending and control criteria, as well as applicable corrective actions and required documentation for each QC measure implemented.

a. Instrumental QC: Count check source(s) for a predetermined time at frequencies defined in the laboratory quality manual (e.g., daily before each use for proportional, scintillation counters, and gamma spectrometers, or monthly for alpha spectrometers). Record the count rate and plot it on the specific system's control chart. Compare the value with the $\pm 2\sigma$, $\pm 3\sigma$, and/or appropriate tolerance value, and repeat the procedure if the $\pm 2\sigma$ values are exceeded. Corrective action is generally required whenever repeated values fall above or below the established statistical control or tolerance limits.

For instruments that produce spectra (e.g., gamma or alpha spectrometers), analysts may track such parameters as instrument response (count rate or total counts in a given spectral area, peak channel location, or the energy of key photopeaks in the spectrum); difference in channels between two specified peaks; resolution (channel peak width at specified peak height); and certain ratios (e.g., peak-to-Compton ratio). It may or may not be

necessary to track all of these routinely; see Section 7120 for specific recommendations. If the basic parameters are outside limits, it may be useful to evaluate additional parameters.

b. QC of instrument background: Perform a background subtraction count as often as the laboratory quality manual indicates (e.g., weekly or monthly). The duration of background subtraction counts should always be as long as, or longer than, that of any sample from which it will be subtracted. For serial counters, such counts are often performed with each batch of samples. Spectrometry measurements, on the other hand, often benefit from longer, less frequent counts (e.g., weekly or monthly) because these produce more precise estimates of the background for specific peaks or regions of interest.

Check background count results for each detection system as often as the laboratory quality manual indicates (e.g., weekly or monthly). Alternatively, background counts may be checked with each batch of samples, or subtraction backgrounds may be evaluated as background checks. At a minimum, background checks should be frequent and sensitive enough to identify related issues that could compromise sample results.

Monitor background counts via control charts. Such counts may change slightly over time without compromising data quality. If Poisson detection statistics are used to estimate counting uncertainty and detection statistics (see 7020C), the assumption is that the background is stable between sample and background-subtraction counts, and that non-Poisson contributions to the background (e.g., electronic noise, variations in ambient background) are minimal. Comparing the background's observed variability (standard deviation for more recent background counts) to that predicted by Poisson statistics (which may be indicated via error bars for each value) may reveal excess uncertainty and could indicate significant problems with the estimates of uncertainty and detection statistics. Establish appropriate evaluation criteria and corrective actions to be taken if backgrounds exceed established limits.^{4,5,7}

Background QC is instrument-specific. For example, for gamma spectrometry backgrounds, the QC checks and acceptance criteria needed depend on whether the detector is NaI(Tl) or high-purity germanium (see Section 7120).

c. *Negative control samples (method and reagent blanks):* A method or reagent blank is “a sample assumed to be essentially target-analyte-free that is carried through the radiochemical preparation, separation and measurement process in the same manner as a routine sample of a given matrix.”§ Analyze method or reagent blanks as batch QC samples frequently enough to detect deviations in measured radioactivity that represent levels of absolute bias|| that could compromise the use of associated results.

Unless otherwise required by the program, blank samples should be analyzed at the frequencies specified in the quality manual for a given analysis (generally, one per batch or 5%, whichever is more frequent). However, this guideline may be varied to fit the situation. For example, a laboratory with a heavy workload and well-established blank analysis program may find that analyzing blanks at a 5% rate (regardless of batch size) is sufficient to determine whether the data meet established criteria. On the other hand, if a test is run less frequently or there are significant concerns about potential contamination or background control, a higher blank-analysis rate might be better.

Ideally, the blank’s count rate should equal the mean background count rate, and the average of background subtracted blank results should be zero. The distribution’s calculated uncertainty should approximate the combined standard uncertainty (CSU) for the measurement. The measured activity of 19 out of 20 blanks should be less than the critical level.# (See 7020C.) The laboratory should define evaluation and acceptance criteria—and associated corrective actions—in its quality manual and ensure that they are consistent with the data quality requirements of the programs they support.

d. *QC for precision:* The IUPAC Gold Book defines *precision* as the “closeness of agreement between independent test results obtained by applying the experimental procedure under stipulated conditions. Precision may be expressed as the standard deviation.”⁸ The laboratory’s internal precision in performing an analytical procedure can be evaluated by analyzing duplicate aliquots of one or more QC samples with each batch of samples.

Duplicate samples may be submitted to analysts on a single- or double-blind basis to effect such an evaluation. (In single-blind analysis, the analyst is aware that a duplicate sample is present. In double-blind analysis, the analyst should be unaware that any of the samples is a QC sample.) Duplicate samples may have either detectable or nondetectable amounts of radioactivity. Statistical treatment of duplicate results can be used effectively to evaluate control of analytical precision and the adequacy of uncertainty estimates both in the presence or absence of activity.

Unless otherwise required by the program, duplicate samples should be analyzed at the minimum rate specified in the quality

manual (generally one duplicate sample per batch or 5%, whichever is more frequent). This guideline may be varied to fit the situation. For example, Safe Drinking Water Act regulations stipulate more frequent duplicate analyses (e.g., 10%). Similarly, a laboratory with a heavy workload and well-established blank analysis program may find that analyzing duplicates at a 5% rate is sufficient to determine whether the data meet established criteria. On the other hand, if a test is run less frequently or there are significant concerns about the reproducibility of the matrix, a higher duplicate-analysis rate would be prudent.

For results above the detection threshold where counting-related uncertainty is small (e.g., ten times the critical level activity), the absolute difference between duplicate measurements should be less than three times the acceptable standard deviation for the specific analysis (see Table 7020:I).

$$\text{Absolute Difference} = \frac{|AC_s + AC_{dup}|}{u(AC_{target})}$$

where:

AC_s = sample result (e.g., pCi/L),
 AC_{dup} = duplicate sample result (e.g., pCi/L), and
 $u(AC_{target})$ = the targeted combined standard uncertainty of sample result (k=1).

A more robust measure [the normalized absolute difference (NAD)** between two results] evaluates statistical agreement between two results of any magnitude based on their respective uncertainties:

$$NAD = \frac{|AC_s - AC_{dup}|}{\sqrt{u^2(AC_s) + u^2(AC_{dup})}}$$

where:

NAD = normalized absolute difference statistic,
 $u(AC_s)$ = combined standard uncertainty of sample result (k=1),
 and
 $u(AC_{dup})$ = combined standard uncertainty of duplicate sample result (k=1).

If the NAD exceeds 2—the warning limit (i.e., results differ by two standard deviations)††—current and prior measurements are suspect. Examine calculations, control charts, and procedures, and reanalyze samples as necessary. If NAD exceeds 3—the control limit (i.e., results differ by more than three standard deviations)†††—a problem may be indicated. Examine calculations, control charts, and procedures, and re-analyze any samples that have been affected by the problem unless there are indications of sample non-homogeneity that would prevent reproducible laboratory subsampling (e.g., presence of hot particles in the sample).

§ MARLAP glossary.

|| Absolute bias is a persistent deviation of the mean measured net activity of blank results from zero. Check MARLAP.

Blanks with activity exceeding the critical level activity may be recounted a single time to demonstrate that the excursion is due to Poisson variability in the result. If the result of the recount is less than the critical level activity, and examination of the control chart for blanks does not show problems, there is no need to recount associated samples in the batch.

** Also referred to as the duplicate error ratio (DER) or replicate error ratio (RER).

†† Two standard deviations correspond to the 95.4% confidence level and one in twenty results should exceed this criterion. Three standard deviations correspond to the 99.7% confidence level: three in a thousand measurements should exceed this criterion.

Relative percent difference (RPD) is also used to evaluate duplicate results. This measure does not take uncertainty into account, but it does provide useful information for such programs as Safe Drinking Water compliance testing, where only Poisson uncertainty of results is reported.

$$RPD = \frac{|AC_s - AC_{dup}|}{(AC_s + AC_{dup})/2} \times 100$$

where:

RPD = relative percent difference,

AC_s = sample result (e.g., pCi/L), and

AC_{dup} = duplicate sample result (e.g., pCi/L).

The laboratory should define all evaluation and acceptance criteria, and associated corrective actions, in its quality manual and ensure that they are consistent with the DQOs and MQOs of the programs they support. More detailed discussions of QC statistics for duplicates is given elsewhere.^{4,5,9}

e. Positive controls (LFBs and matrix spikes): Analytical methods are said to be in control when they produce precise, unbiased results. Two QC measures are commonly used to assess the ongoing accuracy of analytical methods: LFBs and matrix spikes. These QC measures and their evaluation should be defined in the laboratory quality manual.

1) Laboratory-fortified blanks (also called *laboratory control samples*)—Unless otherwise required by the program, LFBs consist of demineralized water spiked with a known activity of a traceable radiostandard and are analyzed at a frequency of one per batch of 20 or fewer samples. The LFB is treated and analyzed just like all the other samples in the batch. Results are compared to known values based on percent recovery:

$$\% \text{ Recovery} = \frac{\text{Observed Result}}{\text{Known Result}} \times 100$$

where:

% Recovery = ratio of observed to known values (%),

Observed result = measured result [expressed in units used to report associated samples (e.g., pCi/L)], and

Known result = theoretical result calculated from the spike added [expressed in the same units used to report associated samples (e.g., pCi/L)].

NOTE: Where possible, the result should be calculated assuming an aliquot size similar to those used for the associated samples.

2) Matrix spikes—Unless otherwise required by the program, prepare one matrix spike per batch of 20 or fewer samples for each method in which no chemical yield carrier or tracer is added to samples. The matrix spike consists of a duplicate aliquot of one batch sample that has been spiked with a known activity of a traceable radiostandard. The sample is processed with the rest of the batch, and results are evaluated based on percent recovery:

$$\% \text{ MS Recovery} = \frac{AC_{MS} - AC_{Smp}}{A_{Spk}/V_{MS}} \times 100$$

where:

% MS Recovery = recovery of the matrix spike from the percent recovery of activity added to the matrix spike sample,

AC_{MS} = measured activity in matrix spike (e.g., pCi/L),

AC_{Smp} = measured activity in original sample (pCi/L),

A_{Spk} = activity added to matrix spike (e.g., pCi), and

V_{MS} = volume of aliquot taken for matrix spike (e.g., L).

3) Evaluation and control charting of LFB and matrix spike results—Laboratories should establish evaluation and acceptance criteria for LFBs and matrix spikes in their laboratory quality manuals. Plot data from these standards or known-addition samples on mean or tolerance control charts^{5,9,10} and determine whether results are within established limits (or if trends, indicate problematic changes in the analytical system). If established control limits are exceeded, investigate results for potential blunders, method bias, or excess uncertainty and take corrective action to address the root cause and prevent recurrence of the problem.

f. Sample-specific QC measures: Additional QC measures are routinely used to assess the quality of radiochemical measurements on a sample-by-sample basis. While batch QCs affect the status of a batch of samples, sample-specific QC only affects the sample in question [unless it is a batch QC sample (e.g., blank, duplicate sample, LFB, or matrix spike)]. Sample-specific QC includes controls on chemical yield or spectral resolution [i.e., full-width-at-half-maximum (FWHM) of observed peaks in spectral results]. The laboratory should define evaluation and acceptance criteria, and associated corrective actions, in its quality manual and ensure that they are consistent with the DQOs of the programs they support.

g. External proficiency testing programs: Laboratories should participate in external proficiency testing programs to ensure that their measurement systems are comparable. For example, to be certified in the United States by EPA (or agreement state) to perform drinking water compliance analyses under the Safe Drinking Water Act, or to be accredited as a NELAC laboratory, a laboratory must participate every 6 months in a proficiency testing (PT) program administered by a nationally accredited PT sample provider. Acceptable performance for each parameter for which the laboratory is (or seeks to be) certified is demonstrated by successful analysis of at least two of the most recent three proficiency samples. Control limits have been established by NELAC. Performance is evaluated by the PT provider. (See Table 7020:I.)

Laboratories are also encouraged to participate in additional intercomparison programs [e.g., the Mixed Analyte Performance Evaluation Program (MAPEP)^{‡‡} and those sponsored by the International Atomic Energy Agency (IAEA)^{§§} and World Health Organization (WHO)].^{||}

h. Selection of radionuclide standards and sources: Confirm that radionuclide standard sources are traceable to the National Institute of Standards and Technology (NIST) or equivalent. Use

^{‡‡} Radiological and Science Laboratory, U.S. Department of Energy, Idaho Operations Office, Idaho Falls, ID.

^{§§} International Atomic Energy Agency, Analytical QC Services, Seibersdorf, P.O. Box 100, A-1400, Vienna.

^{||} World Health Organization, Geneva, Switzerland.

such standard sources, or dilutions thereof, for initial calibration. These sources may be purchased from suppliers listed in annually published buyers' guides. Before purchasing standards from commercial suppliers, inquire whether the radionuclide of interest is traceable to a national standards body (e.g., NIST). Also, consider whether the chemical form and radionuclide purity are adequate.⁴ Examples of radionuclide calibration certificates and NIST traceability certificates have been published (see Table 7020:1).

Calibrated radionuclide standard solutions are prepared for storage and shipment by the supplier in flame-sealed glass ampoules. Perform all dilutions and store radionuclides in well-sealing containers. Only use containers constructed of material that does not adsorb the radionuclides of interest.

Standard sources are radioactive sources with adequate activity and an accurately known radionuclide content and radioactive decay rate (rate of particle or photon emission). Each radionuclide standard should have a calibration certificate containing the following information:

Description:

Principal radionuclide or parameter
Chemical and physical form
Solvent (where applicable)
Carrier identity and concentration
Mass and specific gravity or volume

Standardization:

Activity per mass or volume
Date and time
Method of standardization

Accuracy:

Combined standard uncertainty
Coverage factor/confidence level

Purity:

Activity of decay progeny
Identity and concentration of other impurities and whether they are included in principal activity

Assumptions:

Decay scheme
Half-life and uncertainty
Equilibrium ratios

Production:

Production method
Date of separation

Usable lifetime/expiration date

After preparation and before use, verify the activity concentration of liquid radioactivity standards and tracers by comparing them to a standard obtained from a second, independent source (where possible). Also, verify that levels of impurities will meet the requirements of the method in question. Verification procedures and acceptance criteria should be defined in the laboratory's quality manual.

Use instrument check sources to demonstrate the instrument's continuing stability and, by inference, existing calibrations by evaluating key operating parameters (e.g., checks of detector response and/or energy calibration). The sources should be of sufficient radiochemical purity, the radionuclides should ideally be long-lived enough to permit use over the period of their intended use, and the sources should have enough activity to minimize counting uncertainty. Check sources, however, need not have known disintegration rates (i.e., need not be a traceable standard source).

Standard reference materials are radioactive materials with accurately known radionuclide content or radioactive decay rate (rate of particle decay or radiation emission). They may be used as internal LCSs, internal tracers, or matrix and blind known additions. They should provide traceability to national standards, such as those provided by NIST.

4. References

1. THE NATIONAL ENVIRONMENTAL LABORATORY ACCREDITATION CONFERENCE INSTITUTE. 2003. The NELAC Institute Standard. The National Environmental Laboratory Accreditation Conference Institute, Weatherford, Texas.
2. INTERNATIONAL STANDARDS ORGANIZATION & INTERNATIONAL ELECTROTECHNICAL COMMISSION. 1999. ISO 17025: General Requirements for the Competence of Testing and Calibration Laboratories, International Standards Organization/International Electrotechnical Commission, Geneva, Switzerland. Available from <http://www.ansi.org/>.
3. U.S. ENVIRONMENTAL PROTECTION AGENCY. 2005. Manual for the Certification of Laboratories Analyzing Drinking Water—Criteria and Procedures, Quality Assurance, 5th Edition, EPA-815-R05-004. U.S. Environmental Protection Agency, Cincinnati, Ohio. Also available online at <http://water.epa.gov/scitech/drinkingwater/labcert/#two>. Accessed August 2011.
4. U.S. ENVIRONMENTAL PROTECTION AGENCY. 2004. Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP), EPA 402-B-04-001A. U.S. Environmental Protection Agency, Washington, D.C.
5. KANIPE, L.G. 1977. Handbook for Analytical QC in Radioanalytical Laboratories. E-EP/77-4, TVA, EPA-600/7-77-038, Section 3. U.S. Environmental Protection Agency, Washington, D.C.
6. ANSI N42.22-1995 (R2002), American National Standard-Traceability of Radioactive Sources to the National Institute of Standards and Technology (NIST) and Associated Instrument Quality Control, New York, N.Y.
7. ASTM INTERNATIONAL. 2006. Standard Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements. D7282. ASTM International, W. Conshohocken, Pa.
8. INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY. 1997. Compendium of Chemical Terminology: IUPAC Recommendations, 2nd Edition. (The Gold Book.) A.D. McNaught & A. Wilkinson, eds. Blackwell Science, Oxford, United Kingdom.
9. U.S. ENVIRONMENTAL PROTECTION AGENCY. 2005. Manual for the Certification of Laboratories Analyzing Drinking Water, EPA 815-R-05-004. Office of Ground Water and Drinking Water, Technical Support Center, Cincinnati, Ohio.
10. NATIONAL COUNCIL ON RADIATION PROTECTION AND MEASUREMENTS. 1985. A Handbook of Radioactivity Measurements Procedures, NCRP Rep. No. 58. National Council on Radiation Protection and Measurements, Bethesda, Md.

7020 B. Quality Control for Wastewater Samples

Generally, it is difficult to perform collaborative (interlaboratory) analyses of real-matrix wastewater samples because the composition of elements and solids varies from one facility to the next. The methods included herein have been evaluated via homogeneous samples and are only useful for nonhomogeneous samples after sample preparation (e.g., wet or dry oxidation

and/or fusion and solution) resulting in homogeneity. Reference samples used for collaborative testing may be deficient in radioelements exhibiting interferences because short half-life radionuclides decayed during shipment. Generally, however, analytical methods include steps to eliminate such interferences, even though they may be unnecessary for the reference samples.

7020 C. Statistics

Section 1010B, which discusses statistics applicable to chemical analysis, also applies to radioactivity examinations. However, certain statistical concepts particular to radioactivity measurements are discussed below.

1. Propagation of Uncertainty

It is generally necessary to calculate the uncertainty of a value that is not the result of a single, direct measurement but rather is derived from a number of measurements via a mathematical formula. The uncertainty of each direct measurement is either known or can be computed or otherwise estimated. The combined uncertainty of each calculated result may then be derived mathematically from them. Statistically, this is known as *propagation of uncertainty*.

The propagation of uncertainty typically involves combining the sources of uncertainty associated with determining the concentration of radionuclides in environmental samples (e.g., soil, air, milk, or water). These should include uncertainty for each measurement performed at the laboratory (e.g., sample preparation and subsampling, chemical separations and preparation of the sample test source, and analysis) but should not reflect uncertainty associated with sampling before receipt at the laboratory. Any variable that contributes uncertainty to the final measurement must be considered when evaluating the overall uncertainty of the measurement.

The law of propagation of uncertainty is applicable because variance is an additive property. According to the propagation of uncertainty formula, when noncorrelated quantities are added or subtracted, the total variance equals the sum of the variances of all components that contribute to the measurement's overall uncertainty:

$$u_c^2(A) = u_1^2(A) + u_2^2(A) + u_3^2(A) + \dots + u_n^2(A)$$

Thus, the combined standard* uncertainty (CSU), $u_c(A)$, for a measurement is simply the square root of the variance:

$$u_c(A) = \sqrt{u_1^2(A) + u_2^2(A) + u_3^2(A) + \dots + u_n^2(A)}$$

A number of propagation of uncertainty formulas can be used to determine uncertainties for radionuclide concentrations in

TABLE 7020:II. PROPAGATION-OF-UNCERTAINTY FORMULAS

Model Equation	Uncertainty Expression
$Q = X + Y$ or $Q = X - Y$	$u(Q) = \sqrt{\sigma_X^2 + \sigma_Y^2}$
$Q = aX + bY$ or $Q = aX - bY$	$u(Q) = \sqrt{a^2\sigma_X^2 + b^2\sigma_Y^2}$
$Q = XY$	$u(Q) = XY \sqrt{\frac{\sigma_X^2}{X^2} + \frac{\sigma_Y^2}{Y^2}}$
$Q = \frac{X}{Y}$	$u(Q) = \frac{X}{Y} \sqrt{\frac{\sigma_X^2}{X^2} + \frac{\sigma_Y^2}{Y^2}}$

water (see Table 7020:II). The one most widely used in nuclear counting statistics is the first formula, where X = the total number of counts observed when measuring the sample and Y = the background counts. The propagation and reporting of uncertainty are dealt with in great detail elsewhere.^{12,3}

2. Standard Deviation and Counting Uncertainty

A measurement's variability is described by the standard deviation, which can most accurately be estimated by replicate measurements of the quantity in question. Because replicate measurements of each quantity are impractical for most routine sample measurements, under some circumstances, the standard uncertainty associated with measurements may be estimated based on knowledge of the characteristics of the quantity being measured. For example, a lower boundary on the most significant source of uncertainty for very low-activity measurements, often called *counting uncertainty*, can be estimated based on the radioactivity measurements' inherent variability due to the random nature of radioactive decay, which is described by the Poisson distribution. In the ideal case, the standard deviation (uncertainty) of this distribution for a large number of events (N) equals its square root, or

$$u(N) = \sqrt{N}$$

When the number of counts in a measurement (N) is more than about 20, the Poisson distribution increasingly approximates the normal (Gaussian) distribution. For the measurement of radio-

* See MARLAP, Chapter 18, and the BIPM Guide to Uncertainty in Measurements.

activities very close to background, when there are no other significant non-Poisson contributions to the count uncertainty, this approximation can be used to simplify the computation of standard counting uncertainties and thus may facilitate reasonably accurate estimates of the uncertainty of results without needing to perform replicate counts.†

More often, the variable of concern is the standard deviation of the count rate for a single measurement, R , due to uncertainty (counts per unit time):

$$R = \frac{N}{t}$$

where:

t = the duration of the count.

The standard deviation of the count rate, when the appropriate substitutions are made, can be expressed as follows:

$$u(R) = \frac{\sqrt{N}}{t} = \frac{\sqrt{Rt}}{t} = \sqrt{\frac{R}{t}}$$

In practice, all counting instruments have a background counting rate (R_B) when no sample is present. With a sample of a count rate R_o , the net count rate (R_n) due to the sample is:

$$R_n = R_o - R_B$$

Via uncertainty propagation methods, the standard deviation of R_n (the sample's net count rate) is calculated as follows:

$$u(R_n) = \sqrt{\frac{R_o}{t_o} + \frac{R_B}{t_B}}$$

where:

R_o = the sample's count rate,

R_B = the background subtraction count rate,

t_o = elapsed duration of the sample count, and

t_B = elapsed duration of the background subtraction count.

The duration of the count for a given set of conditions depends on the detection limit required (see below). Preferably divide the count time into equal periods to check the constancy of the observed count rate. For low-level counting, where the net count rate is the same order of magnitude as the background, the background subtraction count should be counted as long as, or longer than, the sample count to which it will be applied. The uncertainty thus calculated includes only uncertainty associated with the radioactive disintegration process' inherent variability and is not the standard deviation of the total analysis. The counting uncertainty is the major portion of the total or combined uncertainty at or near the detection limit. As concentration levels increase, the relative counting uncertainty decreases and

other sources of uncertainty become major contributors to the measurement's combined uncertainty.

To calculate the expanded uncertainty, multiply the standard uncertainty (1σ) by a coverage factor (k) to report uncertainty at different confidence levels.

$$U(AC) = k \times u(AC)$$

where:

$U(AC)$ = expanded combined uncertainty of the activity concentration,

k = coverage factor (e.g., 1.96 for 95% confidence), and

$u(AC)$ = standard uncertainty of the activity concentration.

All radioactivity measurements should be reported with their associated CSUs ($X.XX \pm k \times \text{CSU}$) in appropriate activity concentration units. The respective value for the coverage factor for the uncertainty (k) or the confidence interval should always be clearly reported with the reported uncertainty.

3. Detection Limits

a. Detection decisions: In analyte detection, the *critical value* is defined in MARLAP¹ as:

“The minimum measured value (e.g., of the instrument signal or the analyte concentration) required to give confidence that a positive (nonzero) amount of analyte is present in the material analyzed. The critical value is sometimes called the critical level or decision level.”⁴

Various conventions have been used to estimate the critical value. The procedure recommended here is based on hypothesis testing.^{1,5} If there are no interferences and the observed uncertainty for a representative blank approximates the Poisson uncertainty, then the critical value may be estimated as follows:

$$L_c = K_\alpha \sqrt{\frac{N_B}{t_B \times t_s} \times \left(1 + \frac{t_s}{t_B}\right)} = K_\alpha \sqrt{\frac{R_B}{t_s} \times \left(1 + \frac{t_s}{t_B}\right)}$$

where:

K_α = value for upper percentile of standardized normal variate corresponding to preselected risk of concluding falsely that activity is present when it is not (α),

N_B = total counts during the counting period of a representative blank or background (cpm),

R_B = count rate of a representative blank or background (cpm),

t_B = duration of the count of the representative blank or background (min), and

t_s = duration of the count of a sample (min).

Generally for the 95% confidence level ($\alpha = 0.05$ and $K_\alpha = 1.645$), the amount of radioactivity needed to provide confidence that a positive (nonzero) amount of analyte is present in the analyzed material (i.e., is detected) is

$$L_c = 1.645 \sqrt{\frac{R_B}{t_s} \times \left(1 + \frac{t_s}{t_B}\right)}$$

† This condition should be assured by evaluation of checks of the stability of the background as described in ¶ 3b above. If other sources of uncertainty are present, their contribution to the overall uncertainty should be estimated and accounted for when estimating measurement uncertainties. See MARLAP, Chapter 20.

When the sample and background count duration are equal, the above equation simplifies to:

$$L_c = 2.33 \sqrt{\frac{R_B}{t_s}}$$

This formulation applies only to situations in which a large number of background counts are observed during the counting period (greater than at least 100 counts). For formulations that address, for example, situations commonly encountered during alpha counting (when fewer than at least 100 background counts are observed during the counting period), see Chapter 20 of MARLAP. MARLAP also addresses how to accommodate uncertainty in excess of that predicted by Poisson counting uncertainty.

To convert L_c from counts or count rate to activity concentration, use the same factors for efficiency, yield, ingrowth, decay, abundance, sample volume, and activity conversion that are applied to convert counts or count rate to final results for sample measurement results.

b. Minimum detectable activity:‡ The *minimum detectable activity* (MDA) is the smallest amount of radioactivity in a sample that will yield a net count for which there is a predetermined level of confidence that radioactivity will be measured. Two types of errors may occur when making detection decisions: Type I (false detection) and Type II (false nondetection).

Various conventions have been used to estimate the MDA. In this discussion, MDA and the lower limit of detection (LLD), whose definitions are generally identical, will be considered to be equivalent concepts. The minimum detectable concentration (MDC) is the MDA expressed in terms of activity concentration instead of absolute activity.

The recommended procedure for estimating MDA is based on hypothesis testing.^{1,5} If there are no interferences, and the observed uncertainty for a representative blank approximates the Poisson uncertainty, then the MDA may be approximated (in counts) as follows:

$$\text{MDA} = K_\beta^2 + 2L_c$$

where:

K_β = corresponding value for predetermined degree of confidence for detecting presence of activity (1- β).

If the sample and representative blank or background count durations are not equal, and both Type I and II errors are set to 5% ($\alpha = \beta = 0.05$ and $K_\alpha = K_\beta = 1.645$), then MDA would be:

$$\begin{aligned} \text{MDA} &= 2.71/t_s + 3.29 \sqrt{\frac{N_B}{t_B \times t_s} \times \left(1 + \frac{t_s}{t_B}\right)} \\ &= 2.71/t_s + 3.29 \sqrt{\frac{R_B}{t_s} \times \left(1 + \frac{t_s}{t_B}\right)} \end{aligned}$$

‡ The terms MDA, LLD, and MDC have been used interchangeably. The following discussion will focus on the MDA. Minimum detectable concentration (MDC) is the MDA expressed in terms of activity concentration, as opposed to activity. The lower limit of detection (LLD) is a similar concept to the MDA/MDC.

When the durations of both sample and representative blank or background counts are equal, this simplifies to:

$$\text{MDA} = \frac{2.71}{t_s} + 4.65 \times \sqrt{\frac{R_B}{t_s}}$$

This formulation applies only to situations in which more than at least 100 background counts are observed during the counting period. For formulations that address such situations as those commonly encountered during alpha counting (fewer than about 100 background counts during the counting period) and for recommendations on accommodating uncertainty in excess of that predicted by the Poisson counting uncertainty, see Chapter 20 of MARLAP.

To convert MDA from counts or count rate to concentration, use the same factors for efficiency, yield, ingrowth, decay, abundance, sample volume, and activity conversions that are applied to convert counts or count rate to final results for sample measurement results.

c. SDWA Detection Limit: When radioactivity concentrations are monitored to determine compliance with the Safe Drinking Water Act, the required detection capability is defined in terms of the detection limit [“that concentration which can be counted with a precision of plus or minus 100 percent at the 95 percent confidence level (1.96 σ , where σ is the standard deviation of the net counting rate of the sample)”.⁶ The detection limit is calculated as⁴:

$$DL_{DW} = \frac{1.96^2}{2t_s} \times \frac{\left[1 + \sqrt{1 + \frac{4t_s^2}{1.96^2} \times R_B \times \left(\frac{1}{t_s} + \frac{1}{t_B}\right)}\right]}{\varepsilon \times A \times Y \times I \times V \times D \times F}$$

where:

DL_{DW} = Safe Drinking Water Act detection limit, in units or activity/mass or volume,

R_B = count rate for background subtraction count (cpm),

ε = counting efficiency, (cpm/decay particle),

A = abundance (decay particles per disintegration),

Y = chemical yield (fractional),

I = correction factor for ingrowth (fractional),

V = volume or mass of sample aliquot (e.g., L or g),

D = correction for decay (fractional), and

F = factor for converting from dpm to desired reporting units (e.g., 2.22 dpm/pCi).

4. References

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 2004. Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP), EPA 402-B-04-001A. U.S. Environmental Protection Agency, Washington, D.C.
2. EVALUATION OF MEASUREMENT DATA — GUIDE TO THE EXPRESSION OF UNCERTAINTY IN MEASUREMENT (GUM 1995 WITH MINOR CORRECTIONS). 2008. Joint Committee for Guides in Metrology, 100:2008, International Bureau of Weights and Measures.
3. TAYLOR, B. N. & C. E. KUYATT. 1994. NIST Technical Note 1297, Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results. National Institute of Standards and Technology, Gaithersburg, Md.

4. U.S. ENVIRONMENTAL PROTECTION AGENCY. 2009. Protocol for EPA Evaluation of Alternate Test Procedures for Analyzing Radioactive Contaminants in Drinking Water, Appendix D. U.S. Environmental Protection Agency, Washington, D.C.
5. CURRIE, L.A. 1968. Limits for qualitative detection and quantitative determination—application to radiochemistry. *Anal. Chem.* 68:586.
6. U.S. ENVIRONMENTAL PROTECTION AGENCY. 2000. National Primary Drinking Water Regulations; Radionuclides; Final Rule. 40 CFR, Parts 9, 141, & 142. *Fed. Reg.* 65, No. 236, Part II, U.S. Environmental Protection Agency, Washington, D.C.

7020 D. Calculation and Expression of Results

The results of radioactivity analyses usually are reported in terms of “activity” per unit volume or mass. The SI*-recognized unit for activity is the Becquerel (Bq), which is equal to 1 disintegration per second. In the United States, a commonly used unit for reporting environmental concentrations is the picocurie (pCi), which is equal to 0.037 Bq, 2.22 disintegrations per minute (dpm), or 1×10^{-6} microcuries (μCi).

Specific formulas for calculating activity per volume or mass are presented in the individual methods; while each is specific to the method, they are based on the following general formula:

$$AC = \frac{R_S - R_B}{\varepsilon \times A \times Y \times I \times V \times D \times F}$$

where:

AC = activity per unit volume, in units or activity/mass or volume,

R_S = count rate for the sample count (cpm),

R_B = count rate for background subtraction count (cpm),

ε = counting efficiency (cpm/decay particle),

A = abundance (decay particles per disintegration),

Y = chemical yield (fractional),

I = correction factor for ingrowth (fractional),

V = volume or mass of sample aliquot (e.g., L or g),

D = correction for decay (fractional), and

F = factor for converting from dpm to desired reporting units (e.g., 2.22 dpm/pCi).

The variables' values are method-dependent. Every result must be reported with an estimate of its measurement uncertainty

[i.e., the combined standard uncertainty (CSU)], generally in terms of absolute activity concentration (pCi/L or Bq/kg). Because it is the CSU that determines a result's uncertainty, each result should be rounded based on its uncertainty. Generally, uncertainty is reported to one or two significant figures, and the magnitude of the measured activity adjusted to match the uncertainty's final significant digit. If the uncertainty is reported to two significant figures, a measured result of 0.12345 ± 0.06789 would be reported as 0.123 ± 0.068 . Similarly, a result of $12,345 \pm 6789$ would be reported as $12,300 \pm 6800$.

In general, results should never be censored via comparison to an MDC, LLD, or critical value; positive, zero, and negative results should be reported as calculated (i.e., do not report “not detected,” “ND,” or “less than” values).

The MQOs may also dictate the data reporting format. For example, Safe Drinking Water Act compliance testing regulations require that only the counting uncertainty be reported. Radiochemical data for other programs, however, should be reported with an estimate of the result's CSU, as described above.

The following formula illustrates calculation of counting uncertainty at the 95% confidence level:

$$AC = \frac{1.96 \times \sqrt{\frac{R_S}{t_S} + \frac{R_B}{t_B}}}{\varepsilon \times A \times Y \times I \times V \times D \times F}$$

where:

t_S = count duration for the sample (min),

t_B = count duration for the background subtraction count (min),
and

R_S , R_B , ε , AC , A , Y , I , V , D , and F are as previously defined.

* International System of Units